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TWO-CENTER-EXPANSION SCF CALCULATIONS ON ACETYLENE AND ETHYLENE

by

F. J. Janiszewski, P. G. Lykos,
and Arnold C. Wahl

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TABLE OF CONTENTS

	<u>Page</u>
UNITS AND GLOSSARY	10
SUMMARY	11
I. INTRODUCTION.	12
A. Purpose.	12
B. Approximate Methods and Polyatomic Calculations	12
C. Objectives	13
II. SCF THEORY	14
A. Closed-shell Hartree-Fock Theory.	14
B. A Review of the Expansion Method	15
C. The SCF Equations	19
III. CHARACTERIZATION OF THE TCE METHOD	22
A. The TCE Model.	22
B. The Three-center Nuclear-attraction Integrals.	22
C. Review of Expansion Results	24
D. Characterization of the Method	29
E. TCE Results for Hydrogen	29
IV. TCE WAVE FUNCTION FOR ACETYLENE.	33
A. Electronic Structure and Geometry.	33
B. Basis-set Buildup	33
C. Exponent Optimization	35
D. TCE Results.	36
E. Discussion of the Results	41
V. TCE WAVE FUNCTION FOR ETHYLENE.	47
A. Electronic Structure and Geometry.	47
B. Basis-set Buildup	48

TABLE OF CONTENTS

	<u>Page</u>
C. TCE Results.	49
D. Results for Planar Configuration	52
E. Results for Twisted 90° Configuration.	54
VI. CONCLUSIONS.	56
A. Review of the Results.	56
B. Practicality of the Method.	57
C. Future Applicability.	57
APPENDIXES	
A. Molecular Integrals	59
1. Basis Functions	59
2. Coordinate System	59
3. One-electron Integrals.	59
4. Two-electron Integrals	60
B. IBM-7040 Program Specifications	62
C. CDC-3600 Program Specifications	63
D. TCE Wave Functions for Acetylene.	64
E. Charge-density Plots for Acetylene	66
F. Charge-density Contours for Ethylene.	74
ACKNOWLEDGMENT	77
REFERENCES.	78

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	The TCE Model.	22
2.	Total Charge-density Contours for $^3\Sigma^-$ of NH.	28
3.	Charge-density Contours for Hydrogen at $R = 6.283$ bohrs . .	32
4.	Equilibrium Geometry for Linear Acetylene.	33
5.	Total Energy for Acetylene as a Function of Basis-set Buildup	39
6.	Potential Energy for Acetylene as a Function of Basis-set Buildup	39
7.	Kinetic Energy for Acetylene as a Function of Basis-set Buildup	39
8.	Ionization Potential for Acetylene as a Function of Basis-set Buildup	39
9.	Computed Carbon-Carbon Potential Curve for Acetylene . . .	40
10.	Computed Carbon-Hydrogen Potential Curve for Acetylene . .	40
11.	Charge-density Plots of the Acetylene $3\sigma_g$ Orbital for Various Computed Wave Functions.	45
12.	Equilibrium Geometry for Planar and Twisted 90° Ethylene.	48
A.1.	Coordinate System Used in Computing Molecular Integrals . .	59
E.1.	Total Charge-density Contours for Acetylene.	66
E.2.	Charge-density Contours of $1\sigma_g$ Orbital for Acetylene	66
E.3.	Charge-density Contours of $1\sigma_u$ Orbital for Acetylene	67
E.4.	Charge-density Contours of $2\sigma_g$ Orbital for Acetylene	67
E.5.	Charge-density Contours of $2\sigma_u$ Orbital for Acetylene	67
E.6.	Charge-density Contours of $3\sigma_g$ Orbital for Acetylene	67
E.7.	Charge-density Contours of $1\pi_u$ Orbital for Acetylene	67
E.8.	Charge-density Plots of $1\sigma_g$ Orbital for Three Acetylene Wave Functions.	68
E.9.	Charge-density Plots of $1\sigma_u$ Orbital for Three Acetylene Wave Functions.	68
E.10.	Charge-density Plots of $2\sigma_g$ Orbital for Three Acetylene Wave Functions.	69

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
E.11.	Charge-density Plots of $2\sigma_u$ Orbital for Three Acetylene Wave Functions.	69
E.12.	Charge-density Plots of $3\sigma_g$ Orbital for Three Acetylene Wave Functions.	70
E.13.	Density-difference Plots of $1\sigma_g$ Orbital for Acetylene Wave Functions.	70
E.14.	Density-difference Plots of $1\sigma_u$ Orbital for Acetylene Wave Functions.	71
E.15.	Density-difference Plots of $2\sigma_g$ Orbital for Acetylene Wave Functions.	71
E.16.	Density-difference Plots of $2\sigma_u$ Orbital for Acetylene Wave Functions.	72
E.17.	Density-difference Plot of $3\sigma_g$ Orbital for TCE Wave Function and McLean-Yoshimine Hartree-Fock Wave Function.	72
E.18.	Density-difference Plot of $3\sigma_g$ Orbital for TCE Wave Function and McLean Minimal Basis-set Wave Function.	73
F.1.	Total Charge-density Contours for Planar Ethylene.	74
F.2.	Charge-density Contours of $1a_g$ Orbital for Planar Ethylene	74
F.3.	Charge-density Contours of $1a_u$ Orbital for Planar Ethylene	74
F.4.	Charge-density Contours of $2a_g$ Orbital for Planar Ethylene	74
F.5.	Charge-density Contours of $2a_u$ Orbital for Planar Ethylene	75
F.6.	Charge-density Contours of $1b_{3u}$ Orbital for Planar Ethylene	75
F.7.	Charge-density Contours of $3a_g$ Orbital for Planar Ethylene	75
F.8.	Charge-density Contours of $1b_{2g}$ Orbital for Planar Ethylene	75
F.9.	Charge-density Contours of $1b_{2u}$ Orbital for Planar Ethylene	75
F.10.	Total Charge-density Contours for Twisted 90° Ethylene	75

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
F.11.	Charge-density Contours of $2a'$ Orbital for Twisted 90° Ethylene	76
F.12.	Charge-density Contours of $2a''$ Orbital for Twisted 90° Ethylene	76
F.13.	Charge-density Contours of $1e'$ Orbital for Twisted 90° Ethylene	76
F.14.	Charge-density Contours of $3a'$ Orbital for Twisted 90° Ethylene	76
F.15.	Charge-density Contours of $1e''$ Orbital for Twisted 90° Ethylene	76
F.16.	Charge-density Contours of $2e'$ Orbital for Twisted 90° Ethylene	76

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
I.	SCF Results for $^3\Sigma^-$ of NH at $R = 1.9614$.	26
II.	Spectroscopic Constants for $^3\Sigma^-$ of NH.	27
III.	Overlaps of Various Wave Functions for $^3\Sigma^-$ of NH.	28
IV.	TCE Results for Hydrogen at $R = 6.283$ bohrs Using Parr <u>et al.</u> Basis Set.	30
V.	SCF Results for Hydrogen at $R = 6.283$ bohrs Using Wahl and Das Basis Set.	30
VI.	Best TCE Results for Hydrogen at $R = 6.283$ bohrs.	31
VII.	Equilibrium Geometry for Linear Acetylene	33
VIII.	Bagus <u>et al.</u> Nominal Basis for the 3P State of the Carbon Atom	34
IX.	Summary of Energy Results for the Basis-set Buildup for Acetylene.	36
X.	Properties of Acetylene Wave Function as a Function of Basis-set Buildup.	36
XI.	Summary of Calculated Results for Acetylene	37
XII.	Summary of Orbital Energies for Linear Acetylene	37
XIII.	TCE Wave Function for Acetylene	38
XIV.	Summary of SCF Energies as a Function of Internuclear Distances for Acetylene.	40
XV.	Summary of Molecular Properties as a Function of Internuclear Distance for Acetylene.	41
XVI.	Computed Spectroscopic Constants for Acetylene	41
XVII.	Comparison of Calculated Spectroscopic Constants for Various Systems	44
XVIII.	Equilibrium Geometry for Planar and Twisted 90° Ethylene	47
XIX.	Correlation of the Symmetry Species for the Two Configurations of Ethylene	48
XX.	Summary of Calculated Results for Ethylene	49
XXI.	Summary of Orbital Energies for Planar Ethylene	49
XXII.	TCE Wave Function for Planar Ethylene.	50

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
XXIII.	TCE Wave Function for Twisted 90° Ethylene	51
XXIV.	Computed Molecular Properties for Planar and Twisted 90° Ethylene	51
XXV.	Calculated Energies for Planar and Twisted 90° Ethylene . .	51
D.I.	TCE Wave Functions for Acetylene as a Function of the Carbon-Carbon Internuclear Separation	64
D.II.	TCE Wave Function for Acetylene as a Function of the Carbon-Hydrogen Internuclear Separation.	65

UNITS AND GLOSSARY

Units

Length:	1 au = 1 bohr = 0.529167 \AA
Energy:	1 au = 1 hartree = 27.2107 eV
Unit of charge:	1 au = $1e^- = 4.8030 \times 10^{-10} \text{ esu}$
Dipole moment:	1 au = 2.54158 D
Molecular quadrupole moment:	1 au = $1.3449 \times 10^{-26} \text{ esu-cm}^2$

Glossary of Terms

AO:	Atomic orbital
MO:	Molecular orbital
VB:	Valence bond
LCAO-MO:	Linear combination of atomic orbitals to form molecular orbitals
SCF:	Self-consistent field
OCE:	One-center expansion
TCE:	Two-center expansion
HF:	Hartree-Fock
STO:	Slater-type orbital
GTO:	Gaussian-type orbital
T:	Kinetic energy
V_t :	Total electronic potential energy
V_{ne} :	Nuclear-electronic energy
V_{pcf} :	Nuclear-electronic energy arising from the off-center nuclei
V_{ee} :	Electronic-electronic repulsion energy
V_{nn} :	Nuclear-nuclear repulsion energy
V/T :	Virial theorem
OVC:	Optimal valence configuration
IP:	Ionization potential

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SUMMARY

A prime interest of all chemists is the elucidation of molecular structure. A theoretical determination of molecular structure requires accurate solutions to the nonrelativistic Schrödinger equation. Such solutions for large molecules have not been obtained as yet because of the computational difficulties involved in evaluating the multicenter integrals that arise. Many techniques have been proposed to circumvent the need for these integrals. One technique, which has received little attention, is the two-center-expansion (TCE) method in which expansion basis functions are placed on only two centers of a polyatomic system. It seemed desirable, therefore, to characterize and document this technique for obtaining *ab initio* wave functions for polyatomic systems using Slater-type orbitals (STO's) as expansion functions.

The acetylene and ethylene molecules were selected for analysis by this method. They form an ideal series since they have the same heavy atom skeleton with an increasing number of protons, thereby providing a comprehensive test of the method. A completely optimized TCE, self-consistent-field (SCF), molecular-orbital (MO) wave function was obtained for acetylene using the Hartree-Fock-Roothaan procedure. The final results obtained were -76.7240 hartrees for the total energy and 10.86 eV for the ionization potential. The corresponding experimental values are -77.3605 hartrees and 11.41 eV, respectively. Because of the expense involved in obtaining these results, unoptimized TCE-SCF results were obtained for ethylene. The total energy results obtained were -77.5537 hartrees for planar ethylene. The experimental value is -78.6166 hartrees. The error per proton, which is defined as the deviation from the Hartree-Fock value, divided by the number of protons, for acetylene and ethylene were 0.07 and 0.13 hartrees, respectively.

Analysis of the wave functions and molecular properties indicated that those orbitals not involving a carbon-hydrogen bond in acetylene and ethylene were well represented, but those involving the bond were not well represented. As expected, the major deficiency in all the wave functions was the lack of charge density at the protons. The conclusion reached was that for systems of the type H-A-B-H or A-B-H, the method was useful and practical; however, for the general class of molecules $H_m-A-B-H_n$, the method was not practical.

I. INTRODUCTION

A. Purpose

A primary objective of theoretical chemistry is the accurate prediction of molecular structure, properties, and chemical reactivity. From an ab initio viewpoint, this requires as a first step accurate solutions to the electronic Schrödinger equation,

$$\underline{H}\Psi = E\Psi, \quad (1.1)$$

where \underline{H} is the nonrelativistic electronic Hamiltonian defined as[†]

$$\underline{H} = \sum_i -\frac{1}{2}\nabla_i^2 + \sum_{\beta} \sum_i -\frac{Z_{\beta}}{r_{\beta i}} + \sum_{i \neq j} \frac{1}{r_{ij}}, \quad (1.2)$$

where i and j range over electrons, and β over nuclei, and Z_{β} is the nuclear charge of nucleus β . In Eq. 1.1, the Born-Oppenheimer approximation¹ has been invoked, Ψ is an eigenfunction (wave function) of the electronic Hamiltonian operator, and E the corresponding eigenvalue (the total energy).

B. Approximate Methods and Polyatomic Calculations

Exact solutions to the Schrödinger equation have only been obtained for one- and two-electron systems (for example, H_2^+ , H_2).² However, much progress has been made in the implementation of approximate treatments for systems with more than two electrons. Most of these treatments are based on two general methods: the Heitler-London-Pauling-Slater³ or valence-bond (VB) method, and the Hund-Mulliken⁴ or MO method.

At present, Hartree-Fock MO wave functions are being obtained for third- and fourth-row diatomic molecules^{5,6} by the use of the Roothaan⁷ expansion method. That is, solutions of the pseudo-eigen equation,

$$\underline{F}\phi_i = \epsilon_i\phi_i, \quad (1.3)$$

are obtained using MO's that have been constructed from a truncated set of basis functions, namely,

$$\phi_i = \sum_p C_{ip}\chi_p. \quad (1.4)$$

[†]In atomic units; these units will be used throughout the text and are defined on p. 10.

The extension of such calculations to simple polyatomic systems has been relatively slow because of the need for the two-electron multicenter integral,

$$\langle \chi_a \chi_b | \chi_c \chi_d \rangle = \iint \chi_a^*(1) \chi_b(1) \frac{1}{r_{12}} \chi_c(2) \chi_d^*(2) dv_1 dv_2, \quad (1.5)$$

where 1 and 2 label the electrons, and a, b, c, and d label the different nuclear centers of the system. General-purpose computer programs^{8,9} are only now being developed to evaluate these integrals over STO's. To circumvent the need for these integrals, other techniques such as the use of Gaussian-type orbitals (GTO's) and the one-center-expansion (OCE) method were developed. The usefulness of Gaussian functions was demonstrated by Boys¹⁰ when he showed that all the multicenter integrals could be reduced to single-center integrals. The basic deficiency of these functions is their poor behavior at the nucleus. Experience¹¹⁻¹³ has shown that it generally requires three times as many GTO's as STO's to obtain accurate results. With current computer storage and speed, this appears to be a serious restriction.

The OCE method avoided the need for multicenter integrals by placing functions on only one center of the system. If a complete set of orbitals could be used, the charge density could be represented exactly. In practice, this is not possible; however, with a large number of expansion functions, adequate results for chemically interesting systems have been obtained.^{14,15}

A logical extension of the OCE method is the TCE method in which the expansion functions are placed on only two centers of a polyatomic system. Hoyland¹⁶ first implemented this scheme, using elliptical functions, with initial success on small systems (H_3 and H_3^+), but later results¹⁷ on acetylene indicated that the method was not practical. However, no previous comprehensive application of the TCE method to a homologous series of molecules using STO's has been attempted.

C. Objectives

The objectives of this research are:

1. To characterize and document the TCE method utilizing STO's as expansion functions.
2. To obtain TCE-MO representations of acetylene and ethylene.
3. To compare, where possible, the results for these systems with existing multicenter wave functions and experimental results to calibrate the usefulness of the TCE technique.

II. SCF THEORY

A. Closed-shell Hartree-Fock Theory

Solutions to the nonrelativistic Schrödinger equation, even within the constraints of the Born-Oppenheimer approximation, are rigorously possible for only one- and two-electron systems. In 1928, Hund and Mulliken⁴ introduced the molecular-orbital model of the electronic structure of molecules. The model was primarily used in the interpretation of spectra and not as a method for obtaining approximate wave functions for molecules. In 1929, Lennard-Jones¹⁸ recognized that optimal orbital representations could be obtained for molecules by using a procedure analogous to that developed by Hartree¹⁹ and later modified by Fock²⁰ for atoms. This method, the Hartree-Fock procedure, gives mathematically rigorous equations whose solutions are the best orbital representations for the system.

For an N-electron system, the wave function is written as

$$\Psi(1, 2, \dots, N) = (N!)^{-1/2} \left\{ \Phi_1^1 \Phi_1^2 \dots \Phi_{N/2}^N \right\}, \quad (2.1)$$

where the Φ_i^μ are molecular-spin orbitals defined as

$$\Phi_k^\mu = \phi_k(X^\mu, Y^\mu, Z, S^\mu), \quad (2.2)$$

where k labels the orbital and μ labels the electron. Since we shall be considering a spin-free Hamiltonian (Eq. 1.2), the spin and space parts may be factored to give

$$\Phi_k^\mu = \phi_i(X^\mu, Y^\mu, Z^\mu) S_k(S^\mu), \quad (2.3)$$

where k labels the molecular-spin orbital and i the MO.

Because the electron may exist in two spin states, the Pauli principle²¹ states that each MO may be occupied by not more than two electrons. When all MO's for a given system are doubly occupied, the system is said to be a closed-shell system. A system with half-filled MO's is known as an open-shell system. This type system will not be considered in the present report, and the formalism developed will pertain only to closed-shell systems.

An alternative way of expressing Eq. 2.3, is as a Slater determinant:²²

$$\Psi(1, 2, \dots, N) = (N!)^{-1/2} \begin{vmatrix} \phi_1^1 \alpha(1) & \phi_1^1 \beta(1) & \dots & \phi_{N/2}^1 \alpha(1) & \phi_{N/2}^1 \beta(1) \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ \phi_1^N \alpha(N) & \phi_1^N \beta(N) & \dots & \phi_{N/2}^N \alpha(N) & \phi_{N/2}^N \beta(N) \end{vmatrix}, \quad (2.4)$$

where ϕ_i is the space orbital defined in Eq. 2.3, and $\alpha(i)$ and $\beta(i)$ represent the two spin states of electron i .

B. A Review of the Expansion Method

The expansion form of the Hartree-Fock equations was first proposed by Coulson²³ in 1938. However, the most useful form of these equations was developed in 1951 by Roothaan²⁴ when he cast them in a matrix form suitable for use on an electronic digital computer.

Given a wave function of the form of Eq. 2.4, the ϕ_i 's are expressed as a finite linear combination of suitable atomic orbitals (AO's),

$$\phi_i = \sum_p C_{ip} \chi_p, \quad (2.5)$$

where the χ_p 's are any normalizable one-electron function; that is, they satisfy the condition

$$\int \chi_p^{**}(i) \chi_p(i) dv_i = N, \quad (2.6)$$

where N is normally taken to be unity.

The total electronic energy is given by

$$E = \frac{\int \Psi^* \underline{H} \Psi d\tau^{**}}{\int \Psi^* \Psi d\tau}, \quad (2.7)$$

where \underline{H} is the Hamiltonian operator defined in Eq. 1.2, and Ψ is the wave function defined in Eq. 2.4. After the spin part[§] has been summed, the total energy may be written as²⁴

$$E = 2 \sum_i H_i + \sum_{i,j} (2J_{ij} - K_{ij}), \quad (2.8)$$

where the indices i and j run over the number of occupied molecular orbitals, and the symbols H_i , J_{ij} , and K_{ij} are defined as

$$H_i = \int \phi_i^*(\mu) \left| -\frac{1}{2} \nabla^2(\mu) + \sum_{\alpha} -\frac{Z_{\alpha}}{r_{\alpha\mu}} \right| \phi_i(\mu) dv_{\mu}, \quad (2.9)$$

[†]The asterisk implies complex conjugation.

^{**} $d\tau$ implies integration over the spin and space coordinates of the electron; dv implies integration over the space coordinates only.

[§]The Hamiltonian is spin-free; therefore, the spin part can be summed independently.

where α runs over all the nuclei of the system and μ is the electron label;

$$J_{ij} = J_{ji} = J_{ij}^* = J_{ji}^* = \iint \phi_i^*(\mu) \phi_j^*(\nu) \frac{1}{r_{\mu\nu}} \phi_i(\mu) \phi_j(\nu) dv_\mu dv_\nu, \quad (2.10)$$

and

$$K_{ij} = K_{ji} = K_{ij}^* = K_{ji}^* = \iint \phi_i^*(\mu) \phi_j^*(\nu) \frac{1}{r_{\mu\nu}} \phi_i(\nu) \phi_j(\mu) dv_\mu dv_\nu. \quad (2.11)$$

With the introduction of the form of ϕ_i as given by Eq. 2.5, Eqs. 2.9, 2.10, and 2.11 become, respectively,

$$H_i = \int \sum_p C_{ip} \chi_p^*(\mu) \left| -\frac{1}{2} \nabla^2(\mu) + \sum_\alpha -\frac{Z_\alpha}{r_{\alpha\mu}} \right| \sum_p C_{ip} \chi_p(\mu) dv_\mu dv_\nu, \quad (2.12)$$

$$J_{ij} = \iint \sum_p C_{ip} \chi_p^*(\mu) \sum_q C_{iq} \chi_q^*(\nu) \frac{1}{r_{\mu\nu}} \sum_p C_{ip} \chi_p(\mu) \sum_q C_{iq} \chi_q(\nu) dv_\mu dv_\nu, \quad (2.13)$$

and

$$K_{ij} = \iint \sum_p C_{ip} \chi_p^*(\mu) \sum_q C_{iq} \chi_q^*(\nu) \frac{1}{r_{\mu\nu}} \sum_p C_{ip} \chi_p(\nu) \sum_q C_{iq} \chi_q(\mu) dv_\mu dv_\nu. \quad (2.14)$$

They may be transformed into a more convenient matrix notation by writing the χ 's as a vector,

$$\chi = (\chi_1 \chi_2 \dots \chi_p), \quad (2.15)$$

and the C_{pi} 's as a matrix,

$$\underline{C} = \begin{bmatrix} C_{11} & C_{12} & \dots & C_{1m} \\ \cdot & \cdot & & \cdot \\ \cdot & & \cdot & \cdot \\ \cdot & & & \cdot \\ C_{p1} & C_{p2} & \dots & C_{pm} \end{bmatrix}, \quad (2.16)$$

thereby transforming Eq. 2.5 to

$$\phi_i = \chi \cdot C_i, \quad (2.17)$$

where C_i is defined as a column of matrix \underline{C}

$$C_i = \begin{bmatrix} C_{1i} \\ C_{2i} \\ \vdots \\ C_{pi} \end{bmatrix}. \quad (2.18)$$

Finally, the matrix ϕ may be written as the scalar product between χ and the matrix C ; that is,

$$\phi = \chi \cdot C. \quad (2.19)$$

The total wave function must be orthonormal, which implies that

$$\int \Psi^* \Psi \, dr = \delta_{ij}, \quad (2.20)$$

where δ_{ij} is the Kronecker delta defined as

$$\delta_{ij} = \begin{cases} 1 & \text{for } i = j \\ 0 & \text{for } i \neq j \end{cases}. \quad (2.21)$$

Transforming to integrals over the expansion basis (Eq. 2.5) yields the condition that

$$C_i^\dagger S C_j = \delta_{ij}, \quad (2.22)$$

where S is the overlap matrix whose elements are the integrals

$$S_{ij} = \int \chi_i^*(\mu) \chi_j(\mu) \, dv_\mu. \quad (2.23)$$

Similarly, Eqs. 2.12-2.14 may be transformed to the following matrix form:

$$H_i = C_i^\dagger H C_i, \quad (2.24)$$

$$J_{ij} = C_i^\dagger J_{ij} C_i = C_j^\dagger J_{ij} C_j, \quad (2.25)$$

$$K_{ij} = C_i^\dagger K_{ij} C_i = C_j^\dagger K_{ij} C_j, \quad (2.26)$$

where the elements of the H matrix are defined as

$$H_{pq} = \int \chi_p^*(\mu) \left[-\frac{1}{2} \nabla^2(\mu) + \sum_\alpha -\frac{Z_\alpha}{r_{\alpha\mu}} \right] \chi_q(\mu) \, dv_\mu \quad (2.27)$$

* C_i^\dagger is the adjoint of C_i (i.e., a row vector).

and the elements of the \mathcal{J} and \mathcal{K} supermatrices,[†] respectively, as

$$\mathcal{J}_{pqrs} = \iint \chi_p^{*(\mu)} \chi_r^{*(\nu)} \frac{1}{r_{\mu\nu}} \chi_q(\mu) \chi_s(\nu) dv_\mu dv_\nu \quad (2.28)$$

and

$$\mathcal{K}_{pqrs} = \iint \chi_p^{*(\mu)} \chi_r^{*(\nu)} \frac{1}{r_{\mu\nu}} \chi_q(\nu) \chi_s(\mu) dv_\mu dv_\nu. \quad (2.29)$$

The \mathcal{J}_j and \mathcal{K}_j matrices are defined as

$$\mathcal{J}_j = D_j \cdot \mathcal{J}, \quad (2.30)$$

and

$$\mathcal{K}_j = D_j \cdot \mathcal{K}, \quad (2.31)$$

where the vector D_j is defined as

$$D_j = C_j C_j^\dagger. \quad (2.32)$$

The density matrix \mathcal{D} , is defined as

$$\mathcal{D} = \sum_j D_j. \quad (2.33)$$

\mathcal{H}_j , \mathcal{J}_j , \mathcal{K}_j , and \mathcal{D} are Hermitian matrices.[‡]

Equation 2.11 may be written in matrix notation as

$$E = H^\dagger \cdot D + \frac{1}{2} D^\dagger \cdot \mathcal{P} \cdot D, \quad (2.34)$$

where H is the matrix defined in Eq. 2.27 but written as a supervector,[§] and D is the density matrix defined in Eq. 2.23 and also written as a supervector. \mathcal{P} is a supermatrix defined as

$$\mathcal{P} = \mathcal{J} - \frac{1}{2} \mathcal{K}, \quad (2.35)$$

where \mathcal{J} and \mathcal{K} are the supermatrices defined in Eqs. 2.28 and 2.29, respectively.

[†]A supermatrix is defined as a direct product of two matrices.

[‡]A Hermitian matrix is defined as one satisfying the condition $U^{*T} = U$ where the T implies the transpose.

[§]A supervector is defined as a direct product of two vectors (i.e., a matrix written as a vector).

C. The SCF Equations

When a linear variation is applied to a wave function of the form of Eq. 2.4, the Hartree-Fock or SCF equations are obtained. When a linear variation is applied to ϕ_i , Eq. 2.8 becomes

$$\delta E = 2 \sum_i \delta H_i + \sum_i (2\delta J_{ij} - \delta K_{ij}). \quad (2.36)$$

Substituting the results of Eqs. 2.24-2.26 into Eq. 2.36 yields

$$\begin{aligned} \delta E = & 2 \sum_i \delta C_i^\dagger \tilde{H} C_i + \sum_{i,j} \left\{ \delta C_i^\dagger (2J_i - K_i) C_i + \delta C_j^\dagger (2J_j - K_j) C_j \right\} \\ & + 2 \sum_i C_i^\dagger \tilde{H} \delta C_i + \sum_{i,j} \left\{ C_i^\dagger (2J_i - K_i) \delta C_i + C_j^\dagger (2J_j - K_j) \delta C_j \right\}. \end{aligned} \quad (2.37)$$

Equation 2.37 may be recast as

$$\delta E = 2 \sum_i \delta C_i^\dagger \left\{ \tilde{H} + \sum_j (2J_j - K_j) \right\} C_i + 2 \sum_i \delta C_i^T \left\{ \tilde{H}^* + \sum_j (2J_j^* - K_j^*) \right\} C_i^* \quad (2.38)$$

or

$$\delta E = 2 \sum_i \delta C_i^\dagger \tilde{F} C_i + 2 \sum_i \delta C_i^T \tilde{F}^* C_i^*, \quad (2.39)$$

where \tilde{F} is the Hartree-Fock operator matrix defined as

$$\tilde{F} = \tilde{H} + \sum_j (2J_j - K_j). \quad (2.40)$$

When the variation is imposed on the orthonormality constraint, Eq. 2.22 becomes

$$\delta C_i^\dagger \tilde{S} C_j + \delta C_i^T \tilde{S}^* C_j^* = 0. \quad (2.41)$$

For the energy to reach a minimum, δE must equal zero for any arbitrary variation in ϕ_i . The standard technique for solving this type problem is by the method of undetermined Lagrangian multipliers.²⁵

The procedure is to multiply Eq. 2.41 by an undetermined factor, let it be $-2\epsilon_{ji}$; then

$$-2 \sum_{i,j} \delta C_i^\dagger \approx C_j \epsilon_{ji} - 2 \sum_{i,j} \delta C_i^T \approx^* C_j^* \epsilon_{ij} = 0. \quad (2.42)$$

When this expression is added to Eq. 2.39 a new expression for δE is obtained, which in order to be a minimum must be equal to zero; that is,

$$\delta E' = 2 \sum_i \delta C_i^\dagger \left(\bar{F} C_i - \sum_j \approx C_j \epsilon_{ji} \right) + 2 \sum_i \delta C_i^T \left(\bar{F}^* C_i^* - \sum_j \approx^* C_j^* \epsilon_{ij} \right) = 0. \quad (2.43)$$

The conditions that $\delta E'$ equals zero are that

$$\bar{F} C_i - \sum_j \approx C_j \epsilon_{ji} = 0, \quad (2.44)$$

and

$$\bar{F}^* C_i^* - \sum_j \approx^* C_j^* \epsilon_{ij} = 0, \quad (2.45)$$

or that

$$\bar{F} C_i = \sum_j \approx C_j \epsilon_{ji}, \quad (2.46)$$

and

$$\bar{F}^* C_i^* = \sum_j \approx^* C_j^* \epsilon_{ij}. \quad (2.47)$$

Complex-conjugating Eq. 2.47 and subtracting it from Eq. 2.46 yields

$$\sum_j \approx C_j \epsilon_{ji} = \sum_j \approx C_j \epsilon_{ij}^*, \quad (2.48)$$

or

$$\sum_j \approx C_j (\epsilon_{ij} - \epsilon_{ji}^*) = 0. \quad (2.49)$$

For this to be satisfied,

$$\epsilon_{ji} - \epsilon_{ij}^* = 0, \quad (2.50)$$

or

$$\epsilon_{ji} = \epsilon_{ij}^*, \quad (2.51)$$

which implies that the ϵ_{ij} 's are elements of a Hermitian matrix, and therefore Eqs. 2.46 and 2.47 are equivalent. Equation 2.46 can then be written in matrix form as

$$\tilde{F}\tilde{C} = \tilde{S}\tilde{C}\tilde{E}. \quad (2.52)$$

Because \tilde{E} is a Hermitian matrix, it may be transformed by means of a similarity transformation to diagonal form; that is,

$$\tilde{\epsilon} = U^{*T}EU, \quad (2.53)$$

where $\tilde{\epsilon}$ is a diagonal matrix.

Equation 2.52 may be written in its familiar form as the pseudo-eigen equation,

$$\tilde{F}\tilde{C}_i = \epsilon_i\tilde{S}\tilde{C}_i. \quad (2.54)$$

Equation 2.54 is commonly known as the Hartree-Fock-Roothaan equation.

III. CHARACTERIZATION OF THE TCE METHOD

A. The TCE Model

The electronic Hamiltonian for a polyatomic system was given in Eq. 1.2. Expanding to integrals over an approximate wave function of the form of Eq. 2.5 yielded Eqs. 2.12-2.14. It is easily seen from these equations that placing basis functions on every center of a polyatomic system results in the multicenter integrals defined in Eq. 1.5. However, if basis functions are placed on only two centers of the system (as is done by definition in the TCE method), the only additional integrals to be evaluated, over those that would arise if the system were a diatomic molecule, are the one-electron nuclear-attraction integrals involving the off-center nuclei. It is apparent therefore that ab initio calculations can be made on a large class of polyatomic systems without computing the multicenter integrals of Eq. 1.5. The class of molecules most appropriate for this approach are the type $H_m-A-B-H_n$, where A and B are the heavy expansion centers with m and n protons attached to them respectively. The coordinate system for the TCE model is shown in Fig. 1.

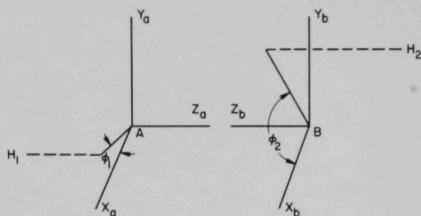


Fig. 1
The TCE Model

B. The Three-center Nuclear-attraction Integrals

The nuclear-attraction integrals that arise in the TCE method are

$$\int \chi_p^{(\mu)} \sum_{\beta} -\frac{Z_{\beta}}{r_{\beta\mu}} \chi_q^{(\mu)} dv_i, \quad (3.1)$$

where β ranges over the number of off-center nuclei, μ labels the electron, and p and q label the basis function, χ . The functions χ used in this work are complex STO's²⁶ defined as

$$\chi_{n\ell m} = (2\xi)^{n+\frac{1}{2}} (2n!)^{-\frac{1}{2}} r^{n-1} e^{-\xi r} Y_{\ell m}(\theta, \phi), \quad (3.2)$$

where n, ℓ , and m are the quantum numbers, and ξ the orbital exponent. The $Y_{\ell, m}(\theta, \phi)$ are the complex spherical harmonics defined as

$$Y_{\ell m}(\theta, \phi) = \mathcal{P}_{\ell m}(\cos \theta) \Phi_m(\phi), \quad (3.3)$$

where the $\mathcal{P}_{\ell m}(\cos \theta)$ are the normalized associated Legendre polynomials and $\Phi_m(\phi)$ is defined as

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}, \quad (3.4)$$

where i represents the imaginary number $(-1)^{1/2}$. This choice of expansion function implies that the molecular orbitals ϕ_i defined in Eq. 2.5 may be either real or complex. In this work, the expansion coefficients are chosen to be real; therefore the ϕ_i are, in general, complex. Their modulus squared, corresponding to the orbital charge density is real; namely,

$$|\phi_i|^2 = \phi_i \phi_i^* = \text{real number}. \quad (3.5)$$

Although the basis functions χ are placed only on two centers of the system, a multicenter integral does arise, namely, the three-center nuclear-attraction integral

$$\int \chi_a(\mu) \sum_{\beta} -\frac{Z_{\beta}}{r_{\beta\mu}} \chi'_b(\mu) d\mathbf{v}_{\mu}, \quad (3.6)$$

where a and b label the expansion centers, and the prime on χ implies that χ and χ' may be different functions. Expression 3.6 may be written, after integrating over the angle ϕ , as⁸

$$I \sum_{\beta} e^{i(m_a - m_b)\phi_{\beta}}, \quad (3.7)$$

where

$$I = \int \chi_a(\mu) \frac{Z_{\beta}}{r_{\beta\mu}} \chi_b(\mu) d\xi d\eta,$$

m_a and m_b are the magnetic quantum number m for χ_a and χ_b , respectively, and ϕ_{β} is the angle ϕ of the off-center atom relative to the diatomic coordinate system (see Fig. 1). One advantage of the TCE method is that the geometry of a system can be investigated rather inexpensively since only the nuclear-attraction integrals arising from the new configuration of off-center nuclei are required, provided the internuclear separation between the expansion centers remains constant. Furthermore, because of the method used for computing these integrals, a rotation of the off-center nuclei by some arbitrary angle ϕ requires negligible computing time.

When the Euler Formula²⁷ is introduced, Expression 3.7 may be rewritten as

$$I \sum_{\beta} \left\{ \cos \left[(m_a - m_b) \phi_{\beta} \right] + i \sin \left[(m_a - m_b) \phi_{\beta} \right] \right\}. \quad (3.8)$$

For these integrals, there are no restrictions on the allowed values of m ; therefore Expression 3.8 can give complex results. As a matter of convenience, however, only real integrals were allowed. The condition to be satisfied for these integrals to be real is that

$$\sum_{\beta} i \sin \left[(m_a - m_b) \phi_{\beta} \right] = 0. \quad (3.9)$$

Imposing this requirement places a restriction on the geometries of a polyatomic system that can be considered.

Detailed information on these and all the integrals that arise in the method are contained in a series of papers by Wahl et al.^{8,28-30} This information is briefly summarized in Appendix A.

C. Review of Expansion Results

The one-center expansion method has received widespread attention the last few years because of its computational simplicity and wide range of applicability.

The basic limitation to the method appears to be economics. Present-day computers have limited storage and computing speed thereby restricting the size of the basis set. It has been discussed³¹ that the major problem with a limited basis set is its inability to adequately represent the charge at the off-center nuclei, namely, the regions in space where $H\psi/\psi$ diverges. The number of these regions in space is equal to the number of nuclei. The size of the region and the extent of the divergence are assumed to be roughly proportional to³²

$$\frac{Z_{\eta}}{\ell_{\min} + 1} \quad (3.10)$$

where Z_{η} is the charge of nucleus η , and ℓ_{\min} is the minimum value of ℓ allowed by the irreducible representation of the molecular-symmetry point group. For hydrides, this quantity has its smallest value, hence, the choice of compounds, $A-H_n$. Furthermore, as the number of regions increases, it becomes more difficult to adequately represent the charge at these centers, and the expansion technique becomes less satisfactory.

The near Hartree-Fock expansion wave functions that have been obtained have had fair success in predicting such properties as susceptibilities, X-ray scattering factors, and geometry. In general, those properties that do not depend upon accurate representation of the charge density in the regions of the off-center nuclei can be predicted with fair accuracy. For the total energy, the important consideration is the size and the number of regions of space where $H\psi/\psi$ diverges, and the extent of the divergence.³²

The first large-scale computation of molecular wave functions on a series of compounds using the OCE technique was done by Moccia.³² With a limited range of harmonics ($l \leq 3$) and limited amounts of basis-set optimization, Moccia obtained reasonable results. Of particular interest are his results for hydrogen fluoride (HF) and methane (CH_4), which were within 0.065 hartree of the total Hartree-Fock energy for hydrogen fluoride and 0.31 hartree for methane. More recent work by Hoyland³³ has shown that the basic deficiency in Moccia's basis sets was the lack of higher spherical harmonics ($l > 3$). Using higher harmonics ($l \leq 8$), Hoyland obtained results within 0.011 hartree of the total Hartree-Fock energy for hydrogen fluoride and 0.116 hartree for methane.

These systems represent extremes in molecular-expansion calculations and therefore constitute excellent test systems. Hydrogen fluoride has a small internuclear separation (1.733 bohrs) with a very polar band, and only one off-center proton. The charge density in the vicinity of the proton is small, making the molecule an ideal system for a one-center expansion. By contrast, methane has a larger internuclear separation (2.0665 bohrs), a nonpolar band, and four off-center protons, thus requiring a much greater effort to represent the charge on the off-centers. Hoyland's results for these two systems represent at least an upper limit to the results obtainable by this technique using a basis set limited by practical considerations.

Sharp-Ritter³⁴ has made a number of calculations on various aromatic fragments. Of interest is her set of calibration calculations on the OH radical. Comparison of her OCE results with the diatomic results of Cade and Huo³⁵ indicate that her results were within 0.07 hartree of the total Hartree-Fock energy and that the ionization potential using Koopmans' approximation³⁶ was better than that obtained using the Cade and Huo results. Plots of her OCE wave function and the two-center wave function of Cade and Huo indicated that the only appreciable deficiency in the charge density was in the region of the proton. Because the outer orbitals were well represented, and because of the speed and flexibility of the method, she was able to make calculations on a wide variety of aromatic-like fragments. With these results, various semiempirical parameters could be calculated, thus giving an ab initio justification for many of the accepted values of these parameters. To make similar full-multicenter calculations would not have been economically possible even if the machinery for doing so had been available.

Calculations aimed at chemical accuracy (within 1-2 kcal) have been performed by Hayes and Parr³⁷ on a number of small systems (H_2^+ , H_2 , H_3^+ , H_3). The results of their studies indicate that the expansion technique can yield accurate results. They demonstrated that to obtain these results very large basis sets with very high n and l values were necessary. They feel that, based on this work, similar results can be obtained for larger systems, and work is proceeding along those lines.

Work by Joshi,¹⁴ Lounsbury,³⁸ and Cade and Huo³⁵ on the NH molecule provide a useful comparison for the present work. Joshi's OCE basis set for NH was a completely optimized set that used the program's full capacity. The basis set was limited, however, to spherical harmonics of $l \leq 3$. The total energy obtained was only 0.07 hartree from the near Hartree-Fock (± 0.001) two-center results obtained by Cade and Huo. Lounsbury built fully optimized, intermediate-size, OCE basis sets, which provide a useful comparison with Joshi's best calculation. Table I contains these results. Lounsbury's energy is within 0.12 hartree of the Hartree-Fock value using 12 basis functions. Joshi, with a set twice as large, obtained results that were only 0.05 hartree better, indicating the apparent slow rate of convergence for an OCE basis set. The ionization potential and dipole moment monotonically change as the basis set is improved. The ionization potential increases, and the dipole moment decreases. The experimental value for the ionization potential is 13.36 eV, which implies that Koopmans' approximation for open shells is not satisfactory. The ionization potential determined by computing the wave functions for the two states is 12.82 eV, which is in satisfactory agreement with experiment. There is no comparison available for

TABLE I. SCF Results for $^3\Sigma^-$ of NH at $R = 1.9614$

Calculation	Total Energy, hartrees	V/T	IP, ^a eV	μ , D
OCE, 4 basis functions ³⁸	-54.5558	-2.0141	11.93	2.492
OCE, 8 basis functions ³⁸	-54.7477	-1.99803	13.69	2.438
OCE, 12 basis functions ³⁸	-54.8588	-2.00025	14.16	2.156
OCE, full set ¹⁴	-54.9060	-	14.37	2.111
Diatomic-Hartree- Fock set ³⁵	-54.9470	-2.00057	14.63	2.078
Experimental ³⁵	-55.252	-	13.10	-

^aIonizational potential using Koopmans' approximation for open shells.

the dipole moment except the computed Hartree-Fock value, and Joshi's results are converging to this value. A comparison of other molecular properties indicates that there is a general progression toward the Hartree-Fock value as the basis set is improved. It is apparent, however, from the work of Joy and Handler,³⁹ Joshi's work on ammonia, and the work of Hoyland mentioned earlier, that these calculations are seriously limited by being restricted to spherical harmonics of $\ell \leq 3$.

Computed spectroscopic constants from Joshi's and Cade and Huo's results are presented in Table II. In general, both results are only in fair agreement with experiment, and in poorer agreement with each other.

TABLE II. Spectroscopic Constants for $^3\Sigma^-$ of NH

Source	B_e, cm^{-1}	α_e, cm^{-1}	ω_e, cm^{-1}	R_e, bohr
Experimental ³⁵	16.668	0.646	[3125.6]	1.9614
OCE, Joshi ¹⁴	17.22	0.8166	3636.8	1.9190
Error, %	+2.8	+27.6		
Diatomic Cade and Huo ³⁸	17.319	0.5715	3556	1.923
Error, %	+3.91	-11.53	+13.75	-1.96

The wave functions may be compared graphically. The charged density for an orbital at any point in space may be given in cylindrical coordinates as

$$\rho_i(Z, r, \theta) = e^- N_i \phi_i(Z, r, \theta) \phi_i^*(Z, r, \theta), \quad (3.11)$$

where e^- is the atomic unit of charge, and N_i is the number of electrons in molecular orbital ϕ_i . The total density, ρ , is defined as

$$\rho(Z, r, \theta) = \sum_i \rho_i(Z, r, \theta). \quad (3.12)$$

The charge on any circle perpendicular to, and centered on, the bond axis (the Z axis) is defined as

$$\rho(Z, r) = \int_{\theta=0}^{2\pi} \rho(Z, r, \theta) d\theta, \quad (3.13)$$

and the average density (namely, the charge on any plane perpendicular to the Z axis) is

$$\rho(Z) = \int_{r=0}^{\infty} \rho(Z, r) r dr. \quad (3.14)$$

Lounsbury made charge-density plots of the various wave functions. They showed that the OCE method tended to build up an excess of charge in the bonding region and a lack of charge on the off-center nucleus. Average charge-density plots also indicated that all the orbitals, except those involved in bonding, are well represented by the OCE method. Overlaps of

the orbitals of the various wave functions with each other confirm this fact. The overlap results are reproduced in Table III.

TABLE III. Overlaps of Various Wave Functions for $^3\Sigma^-$ of NH

Orbital	Lounsbury ^a with Joshi	Lounsbury with Cade and Huo
1 σ	1.00000	1.00000
2 σ	0.99778	0.99474
3 σ	0.99584	0.98991
1 π	0.99986	0.99965

^aTwelve basis functions.

Figure 2 presents total charge-density contour plots for Joshi's OCE result and for the Cade and Huo result. These plots were drawn by the CDC-3600 computer using a program written by Wahl.⁴⁰ These plots also show that there is

a buildup of charge between the centers rather than at the off-center nucleus for the expansion results. That is, the third contour (counting from the nucleus out) for the Cade and Huo wave function passes on the outside of the proton (the right-hand nucleus); for the expansion results, it is approximately replaced by the fourth contour. The third contour is between the two centers. Each contour is 50% of the value of the preceding contour, the innermost contour being the largest ($1 e^-/\text{bohr}^3$).

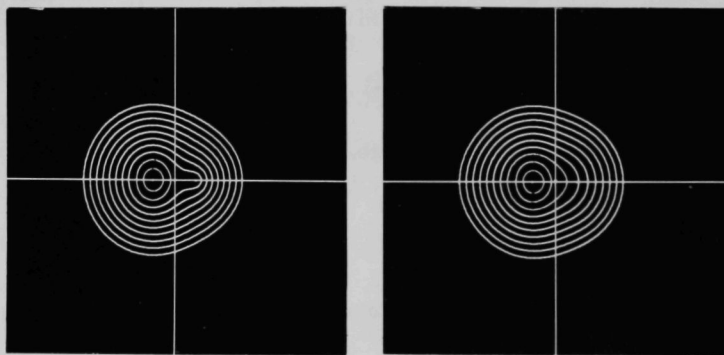


Fig. 2. Total Charge-density Contours for $^3\Sigma^-$ of NH. Left figure is Cade and Huo Hartree-Fock wave function; right figure is Joshi OCE wave function. Largest value plotted = $1 e^-/\text{bohr}^3$; contour ratio = 0.5.

The only published TCE results are those of Hoyland^{16,17} for H_3 , H_3^+ , and acetylene. His results on the small systems were quite encouraging; however, the results for acetylene were not as promising. Hoyland's conclusion was that the use of the TCE method on large molecules was not

justified. However, his use of elliptical orbitals as expansion functions jeopardizes this conclusion somewhat because of inherent difficulties in the use of these functions.⁴¹ The use of STO's as expansion functions overcomes most of these difficulties. Thus TCE wave functions constructed from STO's might be more appropriate in judging the method.

D. Characterization of the Method

The primary purpose of this research was to test the feasibility of the TCE method for large systems. To approximately determine an upper limit to the error inherent in the method (within the constraints of the program limitations), a series of SCF calculations using the IBM-7040 program was performed on the hydrogen molecule. Instructions on the use of the program are contained in Appendix B. The program itself is a modified version of the IBM-7090 homonuclear diatomic program of Wahl, which has been described elsewhere³⁰ and will not be repeated here. The major modification is the inclusion of the new integrals arising in the method.

The basis functions used are symmetry-adapted complex STO's centered on the expansion centers (i.e., A-B). These functions are defined as

$$\chi_{n\ell m} = \frac{1}{\sqrt{2}}(\chi_{a n\ell m} + \sigma \chi_{b n\ell m}), \quad (3.15)$$

where the χ 's are imaginary STO's described by quantum numbers n , ℓ , and m and are centered on a nucleus a or b .

For gerade symmetry, σ is defined as

$$\sigma = (-1)^m, \quad (3.16)$$

and for ungerade symmetry, as

$$\sigma = (-1)^{m+1}. \quad (3.17)$$

The expansion centers chosen were not coincident with the hydrogen nuclei but were chosen to be 2.281 bohrs apart (the carbon-carbon distance in acetylene), with the hydrogen nuclei 2.002 bohrs from each expansion center (the carbon-hydrogen distance in acetylene). Effectively this is the same as considering the hydrogen molecule with an internuclear separation of 6.285 bohrs. The expansion centers had zero charge and therefore served only as points in space where the basis functions were centered.

E. TCE Results for Hydrogen

The initial choice of a basis set was taken from the work of Parr and co-workers⁴² on the hydrogen atom. They attempted to represent the

charge density on the atom from an off-center position with a wave function of the form

$$\psi = C_1(s) + C_2(s') + C_3(p) + C_4(d) + C_5(f) + C_6(g), \quad (3.18)$$

where the C 's are the linear expansion coefficients, and s , p , d , f , and g represent STO's with l equal to 0, 1, 2, 3, and 4, respectively. Their results for a separation of 2 bohrs between the expansion center and the hydrogen nuclei was -0.46056 hartree or approximately 92.1% of the correct result. When this set was used with the omission of the first and last terms, the results given in Table IV were obtained.

TABLE IV. TCE Results for Hydrogen at $R = 6.283$ bohrs
Using Parr *et al.* Basis Set⁴²

Basis Function	Orbital Exponent	Orbital Coefficients	Orbital Energy, hartrees	Total Energy, hartrees
5s	2.200	0.72194	-0.23873	-0.66514
4p	1.700	-0.43161		
5d	2.200	0.37916		
6f	2.600	-0.04990		

To have a benchmark for comparison, an SCF solution for the hydrogen molecule at $R = 6.285$ bohrs was obtained. The basis set chosen was that published by Wahl and Das⁴³ in their OVC studies of hydrogen. The basis set was not reoptimized at the larger internuclear distance. It was felt, however, that this set would give a reasonable upper bound to the solution. The results of this calculation are presented in Table V.

TABLE V. SCF Results for Hydrogen at $R = 6.283$ bohrs
Using Wahl and Das Basis Set⁴³

Basis Function	Orbital Exponent	Orbital Coefficients	Orbital Energy, hartrees	Total Energy, hartrees
1s	0.965	0.47355	-0.31271	-0.811201
1s	2.43	0.11192		
2s	1.16	0.44003		
2p	1.87	0.00926		

The Parr *et al.* set yielded a total energy that was approximately 82% of the correct results (the results presented in Table V). To see if the results could be improved, we made a systematic and exhaustive study. All possible combinations of functions with the correct symmetry and within program limitations were tried. The results of this study were then

condensed down to a small number of basis-set combinations, which were then optimized. These results are presented in Table VI. A total energy that was approximately 91% of the correct value was the best result obtained. This agrees quite well with Parr's 92%[‡] at a similar internuclear distance (i.e., the distance from the expansion center to the off-center nucleus). The present calculations were limited to using functions with ℓ values less than or equal to three. Parr's results, using a set truncated at ℓ equal to three, gave only 88.4% of the correct value. We feel, therefore, that our results represent a good estimate of the TCE results one can obtain for this system with a limited basis set. This opinion is further justified by the convergence of our results as the size of the basis set is increased.

TABLE VI. Best TCE Results for Hydrogen at $R = 6.283$ bohrs

Set Number	Basis Function	Orbital Exponent	Orbital Coefficients	Orbital Energy, hartrees	Total Energy, hartrees	Percentage of IP	Percentage of SCF Results
I	2s	0.681	0.76805	-0.29089	-0.721630	93.02	88.96
	2p	0.700	0.53354				
	3s	1.00	-1.41284				
	3p	0.956	-0.39558				
	5d	1.90	-0.49237				
II	4s	1.4095	0.64432	-0.28683	-0.725125	91.72	89.38
	4p	2.2323	-0.14827				
	5d	1.9087	0.46021				
III	4s	1.4095	0.64076	-0.29062	-0.734281	92.94	90.5
	4p	2.2323	-0.16916				
	4f	1.000	-0.10254				
	5d	1.9087	0.50160				
IV	4s	1.41	0.64578	-0.29192	-0.734721	93.35	90.6
	2p	1.21 ^a	-0.11990				
	2p	2.23 ^a	0.02572				
	4p	2.23	-0.08490				
	4f	1.00	-0.10316				
	5d	1.91	0.49613				

^aNot optimized.

Our purpose was not to obtain the best TCE results for this system, but only to determine an upper limit to the error in the method and also to gain some experience in the selection of basis functions.

The upper limit to the error inherent in the method is defined as

$$\begin{aligned}
 E_{\text{error}} &= E_{\text{correct}} - E_{\text{TCE}} \\
 &= -0.811201 - (-0.734721) \\
 &= -0.0765 \text{ hartrees}
 \end{aligned}
 \tag{3.19}$$

[‡]Hayes and Parr⁴⁴ have extended this work to include more terms with higher ℓ values. His new results are approximately 99.9% of the correct results. However, for comparative purpose, the older results with its limited range of ℓ values are more suitable.

The error per proton may then be defined as

$$E_{\text{error}}/n = -0.0765/2 = -0.0382 \text{ hartree.} \quad (3.20)$$

To see graphically if the TCE method had the same characteristics as the OCE method, we made contour-density plots of the correct SCF results and the TCE results (set number IV in Table VI). These results are presented in Fig. 3 for the SCF results and TCE results. Comparing the two plots, we see that the SCF result has one contour encircling both nuclei, whereas the TCE result has the two outermost contours encompassing both. More important is the lack of the two inner contours in the TCE results that are present in the SCF results. The main characteristic of OCE results is thus displayed by TCE results, namely, the buildup of charge in the bonding region and a deficiency of charge at the off centers.

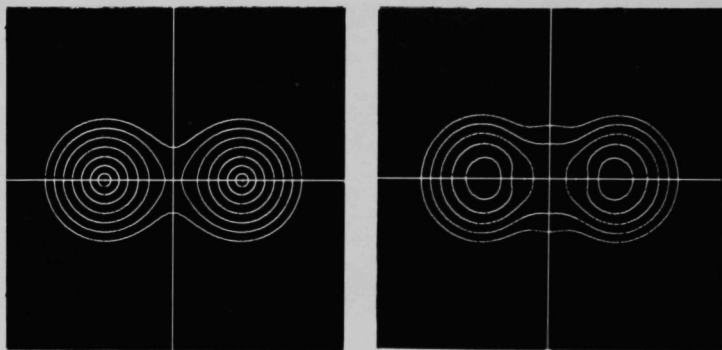


Fig. 3. Charge-density Contours for Hydrogen at $R = 6.283$ bohrs.
Largest value plotted = $0.125 \text{ e}^-/\text{bohr}^3$; contour ratio = 0.5 .

IV. TCE WAVE FUNCTION FOR ACETYLENE

A. Electronic Structure and Geometry

SCF calculations using the symmetry-adapted IBM-7040 program⁹⁰ were performed on the ground state ($1\Sigma_g^+$) of linear acetylene. In this configuration, the molecule belongs to the point group $D_{\infty h}$ and has the electronic configuration

$$1\sigma_g)^2 1\sigma_u)^2 2\sigma_g)^2 2\sigma_u)^2 3\sigma_g)^2 1\pi_u)^4. \quad (4.1)$$

In the ground state, it is a closed-shell configuration and is isoelectronic with the diatomic molecule nitrogen. The internuclear distances were obtained from Herzberg⁴⁵ and are 2.281 and 2.002 bohrs for the carbon-carbon bond and the carbon-hydrogen bond, respectively. The coordinates for the equilibrium geometry are presented in Table VII and shown graphically in Fig. 4. The basis set was optimized at these internuclear distances.

TABLE VII. Equilibrium Geometry for Linear Acetylene⁴⁵

Atom	X Coordinate	Y Coordinate	Z Coordinate
C ₁	0	0	0
C ₂	0	0	2.281
H ₁	0	0	-2.002
H ₂	0	0	4.283

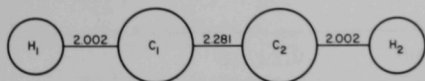


Fig. 4. Equilibrium Geometry for Linear Acetylene

B. Basis-set Buildup

A procedure for obtaining the best molecular wave function from a given size basis set has been determined by Gilbert and Wahl⁴⁶ and the molecular group at The University of Chicago.⁴⁷ It was felt, however, that it would be worthwhile to investigate the use of diatomic results as starting points for the polyatomic calculations. The procedure adopted was to take basis set⁴⁸ for the carbon molecule and replace certain functions with the functions most useful in representing charge on the off-center protons obtained from the TCE hydrogen studies. It became apparent after a number of runs that this approach presented serious problems. They were:

1. The added basis functions actually replaced functions in the original set rather than supplementing them. Thus the quality of the starting set was unknown.
2. The basis set was optimized at a different internuclear distance.

3. Basis sets with approximately the same total energy, but built from different starting sets, had different molecular properties.
4. There are no well-documented rules for building the basis set.

These problems contributed to an uncertainty in the convergence of the results. There could be no guarantee that the best possible wave function would be obtained within the program limitations. It was evident, therefore, that it would be necessary to systematically construct the best possible wave function. The best technique^{46,47} is to take an appropriate atomic basis set for each atom, supplement this set with "polarization" functions, and completely optimize the orbital exponents. For the TCE method, this procedure was modified to also include functions whose main purpose was to represent charge at the off-center nuclei.

The starting atomic set chosen was the nominal set of Bagus *et al.*⁴⁹ for 3P state of the carbon atom. (See Table VIII.) This set was essentially a triple zeta set, namely, four *s* type functions and three *p* type functions. The total energy for the 3P state of carbon using this basis set differed by only 0.00007 hartree from the most accurate set. This set was then supplemented with $\ell \geq 2$ polarization functions, the initial choice of orbital exponents being taken from those used in the basis set for the carbon molecule.

TABLE VIII. Bagus *et al.* Nominal Basis for the 3P State of the Carbon Atom

Basis Function	Orbital Exponent	Orbital Coefficients		
		1S	2S	2P
1S	5.385	0.92300	-0.22226	
1S	9.153	0.08367	-0.00604	
2S	1.428	-0.00049	0.77062	
3S	3.076	0.00373	0.28311	
2P	1.150			0.64975
2P	2.177			0.39516
2P	5.152			0.02472
Orbital energies ^a		-11.32541	-0.70553	-0.43328
Total Energy:		-37.68855		

^aIn atomic units.

Functions with high *n* and ℓ value were then added to represent the charge in the region of the off-center nuclei. The choice of high *n* and ℓ values was based upon the experience gained in the calculations on hydrogen and the preliminary studies on acetylene. Furthermore (as has been discussed), various workers have shown that functions with high *n* and ℓ value are important in the OCE method. The trial orbital exponents

were chosen so that the radial maxima of these functions would occur in the vicinity of the off-center nuclei. This value was determined by differentiating the radial part of the STO with respect to r and setting it equal to zero to obtain a maximum. Namely,

$$\frac{dNr^{n-1}e^{-\zeta r}}{dr} = 0, \quad (4.2)$$

$$(n-1)r^{n-2}e^{-\zeta r} - \zeta r^{n-1}e^{-\zeta r} = 0,$$

$$(n-1)r^{n-2} = \zeta r^{n-1},$$

and

$$\zeta = \frac{n-1}{r}. \quad (4.3)$$

Because of program-capacity restrictions, the optimal placement of these basis functions had to be determined. It was possible to place either one function in σ_g symmetry and one in σ_u symmetry, or three functions in σ_g symmetry. Because the $3\sigma_g$ orbital is basically the bonding orbital, the latter choice was felt to be the best. This choice was later substantiated by removing the functions from σ_g symmetry, placing them in σ_u symmetry, and computing the total energy. The results for this arrangement showed little improvement over the set with these functions completely removed. With the functions in σ_g symmetry, however, the energy was substantially lower.

C. Exponent Optimization

The optimization of the orbital exponents is an important process in obtaining the best possible solution. For a complete minimization of the energy, the exponents of all basis functions should be varied simultaneously.⁵⁰ A procedure for doing this economically has not been worked out, however. Therefore, in lieu of this, single optimizations of each exponent were performed. Presumably, if the optimizations are done in a suitable order, we can expect to obtain a result comparable to the complete optimization method. However, there is no straightforward way to determine the best procedure. The procedure adopted was to first optimize those functions that were most important to the inner orbitals and then those most important to the outer orbitals. The criterion for basis-function importance was the magnitude of its expansion coefficient in that molecular orbital. All exponents were singly optimized once. For economic reasons, no reoptimizations were performed. The running time for a single optimization run on the IBM-7040 was approximately 2 hr. A minimum of four runs were necessary to optimize a single exponent. Thus only a single optimization could be performed on each exponent.

The best value for the exponent was determined by incrementing the orbital exponent (in general a 5-10% increment of the original value was used) until a minimum energy value was determined and bracketed by two points. These points were then fitted with a second-order polynomial and the optimum exponent determined from it. Wahl and the Chicago group used approximately the same method and showed that it led to an error of no more than 0.001 hartree in the final results. The results obtained for acetylene were accurate to at least 0.005 hartree with respect to the best possible results obtainable within the program limitations.

D. TCE Results

The final energy results for various stages of the basis-set buildup are presented in Table IX. The wave functions reported have been computed accurately to one part in 10^4 in the expansion coefficients, and the total energy to at least 10^{-6} hartree. The final wave functions are presented in Appendix D. Various molecular properties computed with these wave functions are presented in Table X. Included when available are the experimental values for these properties.

TABLE IX. Summary of Energy Results for the Basis-set Buildup for Acetylene

Set Number	Basis Functions			Functions Added			Ionization ^b Potential, hartrees	Kinetic Energy, hartrees	Potential Energy, hartrees	Total Energy, hartrees
	σ_g	σ_u	π_u	σ_g	σ_u	π_u				
I ^a	1S 1S' 2S 3S 2P 2P' 2P''	1S 1S' 2S 3S 2P 2P' 2P''	2P 2P' 2P''				0.39837	76.6005	-153.099	-76.4981
II	Set I optimized						0.38831	76.5850	-153.125	-76.5396
III	Set II			3d	3d	3d	0.39810	76.4799	-153.069	-76.5891
IV	Set III optimized						0.39492	76.5020	-153.114	-76.6120
V	Set IV			4f	4f	4f	0.40330	76.5481	-153.238	-76.6896
VI	Set V optimized						0.40552	76.5144	-153.212	-76.6979
VII	Set VI			6p 6d 6f			0.40621	76.5300	-153.241	-76.7111
VIIIC	Set VII optimized						0.40043	76.5671	-153.291	-76.7235

^aGilbert-Bagus nominal 3p carbon atom set. See Table VII.

^bComputed by Koopmans' approximation.⁵¹

^cFinal basis set.

TABLE X. Properties of Acetylene Wave Function as a Function of Basis-set Buildup

Basis-set Number ^a	Virial Theorem	Ionization Potential, ^b hartrees	Identity	Quadrupole q , e^2/bohrs^3	Moment Q , $\times 10^{-26}$ esu	$\langle r_p^{-2} \rangle$, bohrs^2	Diamagnetic Susceptibility χ_L , bohrs ³
I	-1.99866	0.39837	14.0001	87.6603	13.0982	79.8627	-10.2754
II	-1.99941	0.38831	14.0000	88.7548	12.3622	78.5366	-10.0544
IV	-2.00144	0.39810	14.0001	91.9176	10.2353	79.0518	-10.1403
VI	-2.00240	0.40552	14.0001	96.5965	7.0889	79.0518	-10.1403
VIII	-2.00204	0.40043	14.0001	94.6667	8.3866	78.8780	-10.1113
Experimental	-	0.4193 ⁵²	-	-	-	5.01 ⁵³ 3.0 ⁵⁴	-

^aSee Table IX.

^bCalculated using Koopmans' approximation.⁵¹

Table XI contains the best TCE results along with other published calculations on linear acetylene. Table XII lists the orbital energies for these calculations. Table XIII contains the best TCE wave function.

Figures 5-7 are plots of the total, potential, and kinetic energies, and Fig. 8 is a plot of the ionization potential, all as functions of the basis-set buildup.

Charge-density contours of the total density and all the orbital densities are presented in Appendix E. Also included in this appendix are charge-density plots along the z axis for the best TCE wave function and for McLean's minimal and Hartree-Fock wave functions.

TABLE XI. Summary of Calculated Results for Acetylene

Investigator	Type of Calculation ^a	Ionization Potential, ^b hartrees	Total Energy, hartrees
McLean ⁵⁵	Minimal STO	0.44130	-76.54383
McLean and Yoshimine ⁵⁶	Hartree-Fock STO	0.41037	-76.8540
Griffith and Goodman ⁵⁷	Minimal STO	0.394	-76.682
Palke and Lipscomb ⁵⁸	Minimal STO	0.4056	-76.6165
Moskowitz ⁵⁹	Gaussian	0.4023	-76.760
Buenker, Peyerimhoff, and Whitten ⁶⁰	Floating Gaussian	0.4131	-76.7916
Hoyland ¹⁷	TCE, Elliptical	0.3951	-76.6668
Present calculation	TCE, STO	0.3993	-76.7240
Experimental		0.4193 ⁶¹	-77.3605 ⁵⁹

^aAll but the last two reported calculations are multicenter treatments.

^bComputed using Koopmans' approximation.⁵¹

TABLE XII. Summary of Orbital Energies^a for Linear Acetylene

Orbital	TCE	Hoyland ¹⁷	McLean ⁵⁵ Minimal	McLean ⁵⁶ Hartree-Fock	Palke and Lipscomb ⁵⁸	Whitten ⁶⁰
1 σ_g	-11.22490	-11.2504	-11.39977	-11.24407	-11.2978	-11.2585
1 σ_u	-11.22116	-11.2468	-11.39707	-11.24035	-11.2951	-11.2548
2 σ_g	-1.01589	-1.0432	-1.04135	-1.02964	-1.0048	-1.0406
2 σ_u	-0.74270	-0.7604	-0.77576	-0.76985	-0.7513	-0.7658
3 σ_g	-0.65752	-0.6762	-0.68265	-0.68279	-0.6563	-0.6835
1 π_u	-0.40043	-0.3951	-0.44130	-0.41037	-0.4056	-0.4131

^aIn atomic units.

TABLE XIII. TCE Wave Function for Acetylene

Symmetry-adapted Basis Functions		Orbital Coefficients			
Quantum Numbers	Orbital Exponents	$1\sigma_g$	$2\sigma_g$	$3\sigma_g$	$4\sigma_g$
1S	5.32646	0.89735	0.22595	0.06525	0.00724
1S	8.65300	0.10932	0.01386	-0.02399	-0.02253
2S	1.57656	-0.00088	-0.45897	0.37363	-0.97706
3S	2.87600	0.00563	-0.39302	0.22042	0.51050
2P	1.13634	0.00075	-0.07272	-0.35808	6.26205
2P	2.07700	0.00140	-0.18097	-0.29219	-3.65394
2P	3.55200	-0.00122	-0.01706	-0.08768	0.63889
6P	2.76540	-0.00129	0.16552	-0.47324	-2.71497
3d	1.49307	0.00316	-0.10865	0.01157	-0.17920
6d	2.43374	-0.00295	0.09818	-0.07274	0.21450
4f	1.70754	-0.00001	-0.02663	0.02066	0.51743
6f	2.80000	-0.00013	0.08736	-0.24612	-0.42846
Orbital energies, hartrees		-11.22490	-1.01589	-0.65752	0.29741
		$1\sigma_u$	$2\sigma_u$	$3\sigma_u$	$4\sigma_u$
1S	5.34615	0.90901	0.25191	0.24575	0.71103
1S	8.85300	0.09854	-0.02194	-0.00029	-0.16590
2S	1.22800	0.00263	0.76658	2.08316	10.74037
3S	2.82038	0.00484	-0.12914	-0.88062	-0.87810
2P	1.41437	0.00273	2.13787	0.31755	8.28455
2P	1.96481	-0.00056	-0.96752	0.41404	-3.67589
2P	3.20090	-0.00125	0.14928	-0.21118	0.21709
3d	1.45000	0.00129	0.08902	0.92697	1.12860
4f	1.80974	0.00004	0.20615	-0.18730	0.57119
Orbital energies, hartrees		-11.22116	-0.74270	0.46125	0.67717
		$1\pi_u$	$2\pi_u$	$3\pi_u$	$4\pi_u$
2P	1.17024	0.50965	1.59608	0.12985	0.35945
2P	2.00770	0.33636	-2.00399	-0.35918	-0.79184
2P	4.85200	0.06778	0.90555	0.05260	0.39419
2P	5.75000	-0.02379	-0.60788	-0.03937	-0.25745
3d	2.53462	0.03032	-0.09325	0.89208	0.02418
4f	2.60000	0.01941	0.00012	-0.17038	1.05779
Orbital Energies, hartrees		-0.40043	0.65864	1.83110	3.37706
Total energy = -76.723953 hartrees Potential energy = -153.29168 hartrees					

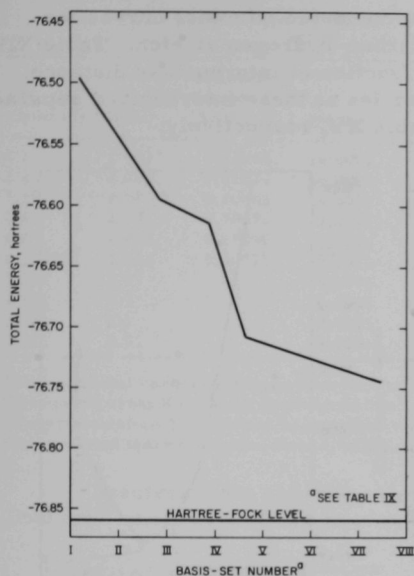


Fig. 5. Total Energy for Acetylene as a Function of Basis-set Buildup

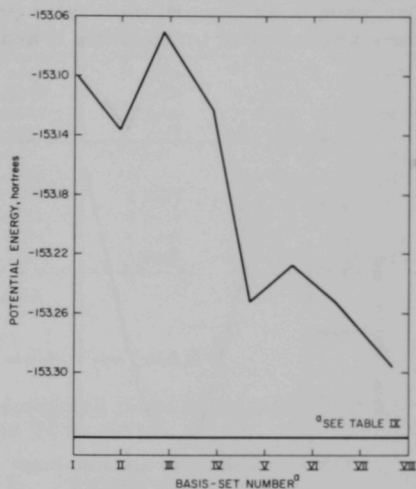


Fig. 6. Potential Energy for Acetylene as a Function of Basis-set Buildup

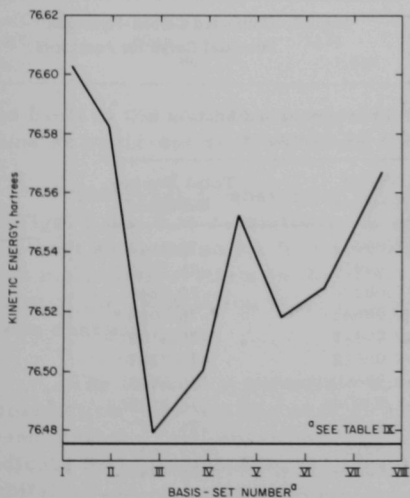


Fig. 7. Kinetic Energy for Acetylene as a Function of Basis-set Buildup

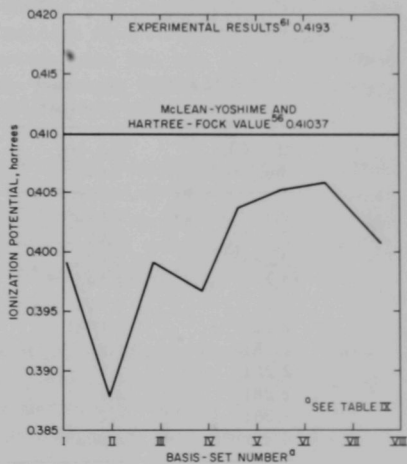


Fig. 8. Ionization Potential† for Acetylene as a Function of Basis-set Buildup

†Computed by Koopmans' approximation.

Figures 9 and 10 are plots of the computed potential curves for the carbon-carbon stretch and for the carbon-hydrogen stretch. Table XIV summarizes the energy quantities as a function of internuclear distance. The wave functions and molecular properties at these internuclear separations are included in Appendix D and Table XV, respectively.

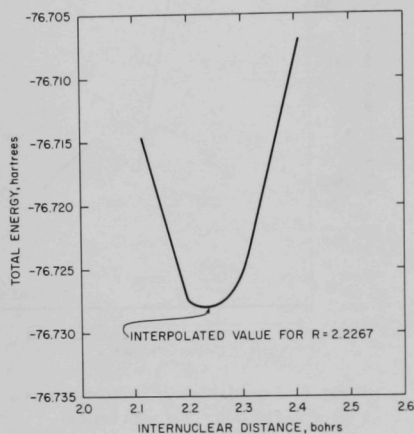


Fig. 9. Computed Carbon-Carbon Potential Curve for Acetylene

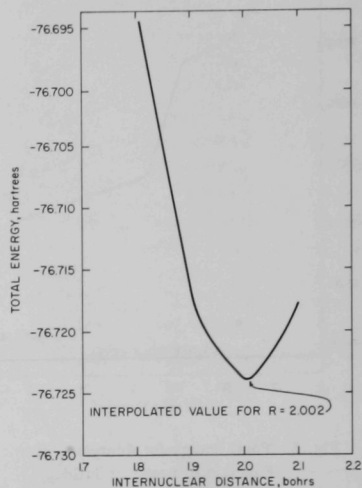


Fig. 10. Computed Carbon-Hydrogen Potential Curve for Acetylene

TABLE XIV. Summary of SCF Energies as a Function of Internuclear Distances for Acetylene

R(C-C), bohrs	R(C-H), bohrs	Virial Theorem	Total Energy, hartrees
2.1	2.002 ^a	-1.99497	-76.7142
2.2	2.002	-1.99919	-76.7256
2.281 ^b	2.002	-2.00204	-76.7240
2.4	2.002	-2.00546	-76.7084
6.0	2.002	-2.00479	-75.8109
2.227 ^c	2.002	-2.00012	-76.7267
2.281	1.8	-1.99690	-76.6943
2.281	1.9	-1.99970	-76.7172
2.281	2.1	-2.00382	-76.7177
2.281	6.0	-2.00147	-75.8631
2.281	2.002 ^d	-2.00204	-76.7240

^aExperimental carbon-hydrogen internuclear distance.

^bExperimental carbon-carbon internuclear distance.

^cInterpolated value for optimal carbon-carbon internuclear distance.

^dInterpolated value for optimal carbon-hydrogen internuclear distance.

TABLE XV. Summary of Molecular Properties as a Function of Internuclear Distance for Acetylene

R(C-C), bohrs	R(C-H), bohrs	Ionization Potential, ^b hartrees	Identity	Quadrupole q, e/bohrs ³	Moment Q, x 10 ⁻²⁶ esu	$\langle r_a \rangle^2$, bohrs ²	Diamagnetic Susceptibility χ_L , bohrs ³
2.1	2.002 ^a	0.42454	14.0001	83.4644	15.9198	72.2400	-9.0050
2.2	2.002	0.41074	14.0001	89.5336	11.8384	75.8611	-9.6085
2.281 ^c	2.002	0.40043	14.0001	94.6667	8.3866	79.8258	-10.2693
2.4	2.002	0.38658	14.0001	102.561	3.0782	83.4498	-10.8733
6.0	2.002	0.23950	14.0002	540.831	-291.645	308.540	-48.3883
2.22670 ^d	2.002	0.40731	14.0001	91.2036	10.7154	76.8463	-9.7727
2.281	1.8	14.0001	14.0001	92.7606	9.6684	77.1637	-9.8256
2.281	1.9	14.0001	14.0001	93.7551	8.9997	78.0267	-9.9694
2.281	2.1	14.0001	14.0001	95.4131	7.8847	79.6307	-10.2368
2.281	6.0	14.0001	14.0001	89.3168	11.9842	84.4998	-11.0483

^aExperimental carbon-hydrogen internuclear distance.^bComputed using Koopmans' approximation.⁵¹^cExperimental carbon-carbon internuclear distance.^dInterpolated optimal carbon-carbon internuclear distance; see Table XIV.

Spectroscopic constants were computed from these curves by a Dunham⁶² analysis and are presented in Table XVI.

TABLE XVI. Computed Spectroscopic Constants for Acetylene

Constant	Computed Value, cm ⁻¹	Experimental Value, ⁴⁵ cm ⁻¹
$\omega_e(\text{C-C})$	2540.6	1974
$\omega_e(\text{C-H})$	6048	3374
B_e	1.206	1.838

E. Discussion of the Results

The energy results for the basis-set buildup as presented in Table IX and the plot of the total energy as a function of this buildup indicate that the total energy is converging but has not yet reached

the limit at the final basis set. However, because of the program restrictions on basis-set size, the limit could not be reached.

The erratic behavior of the potential and kinetic energies plotted in Figs. 6 and 7 is consistent with past experience in diatomic molecules.⁴⁷ The best explanation for this behavior is the poorer approximation to the best molecular orbitals in the intermediate stages and the relative sensitivity of the expectation value of the potential and kinetic energies to these changes.

The ionization potentials computed according to Koopmans'[†] approximation⁵¹ are erratic at first and then seem to follow an increasing trend until the final set, where the value decreases again. This would indicate that this property is also quite sensitive to the changes in the orbitals.

The only safe property to follow to determine the convergence of the results is the total energy. Similar trends for these energy quantities

[†]The ionization potential is approximately equal to the negative value of the orbital energy of the highest-lying, fully occupied molecular orbital.

have also been observed in the construction of basis sets for diatomic molecules. This would indicate that these trends are not unique to the TCE method.

The final results for the present calculation and for other published calculations are represented in Table XI. The best TCE results are between the minimal-multicenter STO and the extensive-multicenter Gaussian treatments.

McLean's Hartree-Fock set is assumed⁶³ to be within 0.002 hartree of the Hartree-Fock value for acetylene. Hence, the error in the TCE calculation is

$$\begin{aligned} E_{\text{error}} &= E_{\text{HF}} - E_{\text{TCE}} = -76.8540 - (-76.7240) \\ &= -0.13 \text{ hartree.} \end{aligned} \quad (4.4)$$

It is difficult to assess exactly what part of this error is in the poorer description of the charge density around the carbon atoms and what part from the description of the charge density in the vicinity of the off-center nuclei. Assuming that the TCE result for the hydrogen molecule at 6.285 bohrs constitutes an upper limit to the error of the description in the vicinity of the protons, we can predict the limit of the calculation. Namely, if we assume that the representation of the charge density in the vicinity of the off-center nuclei for acetylene is equivalent to that for hydrogen, then the total error can be partitioned as

$$E_{\text{error}} = -0.13 \text{ hartree}$$

and

$$E_{\text{maximum error for TCE H}_2} = -0.077 \text{ hartree.} \quad (4.5)$$

Therefore,

$$\begin{aligned} E_{\text{error in the region of the carbon atoms}} &= \\ &= -0.013 - (-0.077) = -0.053 \text{ hartree,} \end{aligned}$$

and

$$E_{\text{limit}} \approx -76.7240 + (-0.053) \approx -76.777 \text{ hartrees.} \quad (4.6)$$

The attempts to represent the off-center nuclei with a limited basis set have introduced an error of approximately the same order of magnitude into the carbon-carbon representation. The estimate for the converged

limit for the TCE calculations within the constraints of basis function type ($n \leq 6$, and $\ell \leq 3$), but not within program capacity, is -76.777 hartrees.

As described earlier, the error increases linearly as the number of off-center nuclei. Empirically for comparative purposes, the error per off-center proton is

$$E_{\text{error}}/2 = -0.13/2 = -0.065 \text{ hartree.} \quad (4.7)$$

This error compares favorably with that reported for the OCE calculations by Joshi on NH and Ritter on the OH radical. The final TCE results represent a lower limit to within 0.005 hartree of the best TCE results that could be obtained with the IBM-7040 program. To obtain the total energy limit would require a much larger basis set. To obtain further improvement would require basis functions with higher n and ℓ values than currently are allowed.

The error in the computed ionization potential may be defined as

$$IP_{\text{HF}} - IP_{\text{TCE}} = 0.41037 - 0.40053 = 0.00984 \text{ hartree,} \quad (4.8)$$

and the actual error as

$$\begin{aligned} IP_{\text{experimental}} - IP_{\text{TCE}} &= 0.4193 - 0.40053 \\ &= 0.0188 \text{ hartree.} \end{aligned} \quad (4.9)$$

Because of the erratic behavior of the ionization potential as a function of basis-set buildup, it is difficult to compare the TCE error in the calculated value with a similar value from any intermediate-size basis set used in producing the Hartree-Fock results for a diatomic molecule. However, comparing the TCE results with those obtained by Joshi for NH, namely,

$$IP_{\text{HF}} - IP_{\text{OCE}} = 0.5376 - 0.5281 = 0.0095 \text{ hartree} \quad (4.10)$$

and

$$\begin{aligned} IP_{\text{experimental}} - IP_{\text{OCE}} &= 0.4814 - 0.5281 \\ &= -0.0467 \text{ hartree,} \end{aligned} \quad (4.11)$$

we see that the difference between the Hartree-Fock value and the OCE computed value is the same as the difference between the Hartree-Fock value and the TCE computed value. The difference between the computed value and the experimental value for the two-center results is 0.019 hartree

or about 4.5% in error. The NH results appear to be in large error; however, the system is an open-shell one and Koopmans' approximation for open-shell systems is not strictly correct. Comparing the acetylene results with the isoelectronic diatomic molecule nitrogen showed the error in the ionization potential for nitrogen to be 10.1%, while for acetylene it was 4.5%. This better agreement with experiment is not unexpected, however, because the Hartree-Fock value for acetylene is only 2.1% in error.

Examination of the molecular properties presented in Table X shows that in general the trend is also erratic as the basis set is improved. Lounsbury's result for NH also exhibited this erratic behavior. The only available experimental property found, other than the ionization potential, was the molecular quadrupole moment. The calculated error was approximately 3.4×10^{-26} esu.

Table XII indicates that those orbitals not involved in the carbon-hydrogen bonding (the $1\sigma_g$, $1\sigma_u$, $2\sigma_g$, and $1\pi_u$) have orbital energies that nearly approximate the Hartree-Fock value. The bonding orbitals, the $2\sigma_u$, and primarily the $3\sigma_g$ orbital have the largest deviation from the Hartree-Fock value. The trend for all the orbital energies is that they are higher than the Hartree-Fock value.

Examination of the spectroscopic constants presented in Table XVI indicates that except for the rotation constant (B_e) the results are poor. This latter constant is quite good since the determined internuclear distances (see Table XIV and Figs. 9 and 10) agree quite well with the experi-

mental values. That the carbon-hydrogen internuclear distance is exactly equal to the experimental value is assumed to be a consequence of our basis set.

TABLE XVII. Comparison of Calculated Spectroscopic Constants for Various Systems

Constant	Calculation	Error, %
ω_e	N_2^{47} (Hartree-Fock)	15.8
ω_e	NH^{14} (OCE)	10.2
$\omega_e(C-C)$	C_2H_2 (TCE)	28.7
$\omega_e(C-H)$	C_2H_2 (TCE)	79.0
B_e	N_2 (Hartree-Fock)	6.1
B_e	NH (OCE)	2.8
B_e	C_2H_2 (TCE)	1.88

Table XVII indicates that our results for the other constants are quite poor in comparison with calculations on other systems. In general, our calculated values are much larger.

The potential curves (Figs. 9 and 10) from which these constants were computed were produced without reoptimization of the basis set at each computed point. It has been shown,⁴⁷ however, that around the minimum there is sufficient flexibility in a large basis so that reoptimization is not necessary.

Before reviewing the poor performance of the TCE wave function, we note that Hartree-Fock potential curves are poor, in general, for spectroscopic constants. Except in special cases, rather than dissociating to the proper mixture of atoms, Hartree-Fock solutions dissociate to a mixture of ions and atoms, thus causing the potential curve to rise more steeply than it should.

Cade and Huo have shown, for the diatomic hydrides A-H, that the Hartree-Fock potential curves give rather good spectroscopic constants. However, the results for homopolar diatomic molecules such as nitrogen are rather poor. The poor performance for acetylene can be rationalized on the basis that at the Hartree-Fock level the results would be quite poor because acetylene is also a homopolar molecule. The results should be even poorer because the TCE calculation is not at the Hartree-Fock level.

To obtain graphically a better idea of the relative quality of the wave function, charge-density plots along the Z axis (bond axis) of the TCE wave function and McLean's wave functions were made. These plots

for the total and orbital densities (presented in Appendix E) show that the TCE orbitals and McLean's orbitals are similar. The major difference occurs in the bonding $3\sigma_g$ orbital. Figure 11 points out that the basic deficiency in an expansion wave function is the lack of charge in the vicinity of the off-center nuclei. The characteristic feature of expansion methods also appears, namely, the buildup of charge in the bonding region. Density difference plots of these results are also presented in Appendix E and graphically point out what was just said. Calculations of the average density (that is, the charge on any plane perpendicular to the Z axis, for the TCE and McLean wave functions) indicate that the same trends are observed. The wave functions are nearly identical in all regions of space except in the carbon-hydrogen bonding region and at the off-center proton.

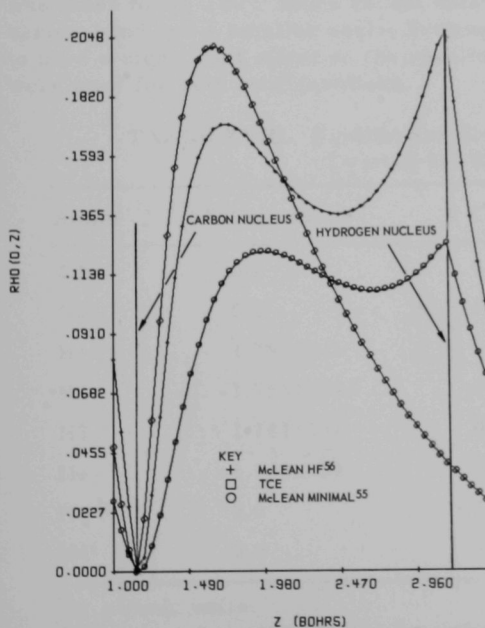


Fig. 11. Charge-density Plots of the Acetylene $3\sigma_g$ Orbital for Various Computed Wave Functions

When compared with the published plots⁴⁰ for the carbon molecule, the contour-density plots of acetylene in Appendix E show that there is a good deal of distortion along the Z axis. The total density has gone from nearly circular contours to elliptical contours. There is no indication, however, of any contours surrounding the protons. Moving out 2.002 bohrs from a carbon atom, we find that in carbon the protons would have been in a region of charge of 0.0625 to 0.03125 e^-/bohr^3 , whereas in acetylene the charge has been distorted so that they are in a region that is between 0.125 and 0.0625 e^-/bohr^3 . All the σ orbitals show this distortion, especially the $3\sigma_g$ bonding orbital. The π molecular orbital has, however, remained relatively the same.

V. TCE WAVE FUNCTION FOR ETHYLENE

A. Electronic Structure and Geometry

SCF-TCE calculations using the CDC-3600 symmetryless TCE program were performed on two configurations of ethylene. The features and limitations of the program are briefly described in Appendix C.

The two configurations considered were the planar and twisted 90° forms. Intermediate positions were not considered since they do not satisfy the condition imposed by Eq. 3.9, namely,

$$i \sum_p \sin(m\phi_p) = 0. \quad (5.1)$$

The coordinates for the equilibrium geometry for the planar and twisted forms are presented in Table XVIII and shown graphically in Fig. 12. The bond lengths used were 2.551 and 2.022 bohrs⁶⁵ for the carbon-carbon and carbon-hydrogen internuclear distances, respectively. The HCH angle was taken to be 120°. More recent data⁶⁶ indicate a slightly shorter carbon-carbon bond and a smaller angle; however, this difference was not expected to have a significant effect on the results. The same bond lengths and angles were used for both configurations.

TABLE XVIII. Equilibrium Geometry^a for Planar and Twisted 90° Ethylene

Atom	X Coordinate	Y Coordinate	Z Coordinate
C1	0.0	0.0	0.0
C2	0.0	0.0	2.5511602
H1	1.7511301	0.0	-1.0110153
H2	-1.7511301	0.0	-1.0110153
H3	1.7511301	0.0	3.5621755
H4	-1.7511301	0.0	3.5621755
H3 ^b	0.0	1.7511301	3.5621755
H4'	0.0	-1.7511301	3.5621755

^aIn atomic units.

^bThe primed coordinates replace the unprimed coordinates for the twisted 90° configuration.

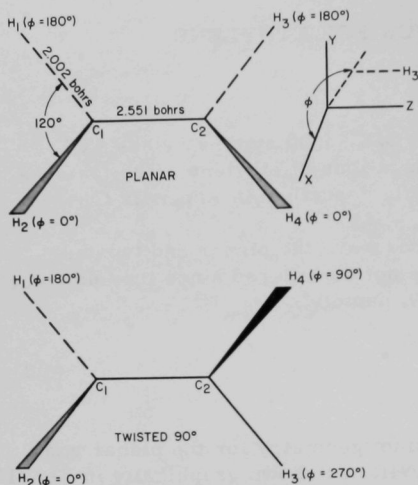


Fig. 12. Equilibrium Geometry for Planar and Twisted 90° Ethylene

The correlation between the symmetry species for the two configurations is presented in Table XIX.

TABLE XIX. Correlation of the Symmetry Species for the Two Configurations of Ethylene

Planar Configuration D_{2h}	Twisted 90° Configuration D_{2d}
a_g	a'
a_u	a''
b_{3u}	e'
b_{2u}	
b_{2g}	e''

B. Basis-set Buildup

The basis set was constructed using an analogous procedure to that described for acetylene. The starting set chosen was the Bagus *et al.*⁴⁹ nominal set for the 3P state of the carbon atom given in Table VIII. To this set was added a $3d\pi$ polarization function with the orbital exponent taken from the acetylene basis set. High n and ℓ value functions, which transformed according to the point group of the molecule, were then added. The orbital exponents for these functions were determined in the same manner as that described earlier for acetylene. The main purpose of these

In the planar configuration, ethylene belongs to the point group D_{2h} and has the electronic configuration

$$1a_g)^2 1a_u)^2 2a_g)^2 2a_u)^2 1b_{3u})^2 3a_g)^2$$

$$1b_{2g})^2 1b_{2u})^2, {}^1A_g, \quad (5.2)$$

which is a closed-shell system isoelectronic with the diatomic molecule oxygen. In the twisted 90° configuration,[‡] the molecule belongs to the point group D_{2d} and has the electronic configuration

$$1a')^2 1a'')^2 2a')^2 2a'')^2 1e')^2 3a')^2$$

$$1e'')^2 2e')^2, {}^1B. \quad (5.3)$$

[‡]This configuration is obtained by twisting one CH_2 group 90° relative to the other CH_2 group.

functions was to represent the charge in the regions of the off-center nuclei. The total number of basis functions chosen was 42. For economic reasons, the same basis set was used for both configurations, and no attempt was made to optimize the set.

C. TCE Results

The final TCE results for the planar and twisted 90° configurations and other published calculations for ethylene are presented in Tables XX and XXI. The wave functions for both configurations have been computed

TABLE XX. Summary of Calculated Results for Ethylene

Investigators	Type of Calculation ^a	Ionization Potential, ^b hartrees	Total Energy, hartrees
Palke and Lipscomb ⁵⁸	Minimal-basis STO	0.3709	-77.8343
Kaldor and Shavitt ⁶⁷	Minimal-basis STO Planar Twisted 90°	0.3691 0.2314	-77.8355 -77.6301
Moskowitz and Harrison ⁶⁸	Gaussian	0.3814	-77.8002
Schulman, Moskowitz, and Hollister ⁶⁹	Contracted Gaussian	0.3736	-78.0062
Ritchie and King ⁷⁰	Contracted Gaussian	-	-77.9483
Buenker, Peyerimhoff, and Whitten ⁶⁰	Floating Gaussian	0.3676	-78.0012
Present calculation	TCE; STO Planar Twisted 90°	0.3560 0.2381	-77.5537 -77.3900
Experimental		0.3852 ⁷¹	-78.6166 ⁷²

^aAll but the last reported calculations are multicenter treatments.

^bComputed using Koopmans' approximation.⁴⁸

TABLE XXI. Summary of Orbital Energies^a for Planar Ethylene

Orbital	TCE	Kaldor and Shavitt ⁶⁷	Palke and Lipscomb ⁵⁸	Moskowitz and Harrison ⁶⁸	Buenker, Peyerimhoff, and Whitten ⁶⁰
1a _g	-11.1953	-11.2794	-11.2875	-11.2395	-11.2341
1a _u	-11.1937	-11.2787	-11.2868	-11.2379	-11.2326
2a _g	-1.0049	-1.0130	-1.0144	-1.0397	-1.0324
2a _u	-0.7574	-0.7815	-0.7823	-0.7959	-0.7987
1b _{3u}	-0.6103	-0.6431	-0.6438	-0.6549	-0.6462
3a _g	-0.5405	-0.5605	-0.5616	-0.5812	-0.5847
1b _{2g}	-0.4618	-0.5054	-0.5061	-0.5145	-0.5064
1b _{2u}	-0.3560	-0.3691	-0.3709	-0.3736	-0.3676

^aIn atomic units.

accurately to one part in 10,000, and the total energy to at least 1×10^{-6} hartree. The final wave functions are presented in Tables XXII and XXIII for the planar and twisted 90° configurations, respectively. Molecular properties were computed with these wave functions and are presented in Table XXIV for the planar and twisted 90° configurations. Various energy expectation values for the two configurations are presented in Table XXV. Charge-density contours of the total density and all the orbitals (in the xz plane only) are presented for both configurations in Appendix F.

TABLE XXII. TCE Wave Function for Planar Ethylene

Basis Functions			Orbital Exponent	Center	Orbital Coefficients									
n	l	m			C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)
1	0	0	5.38200	A	0.65215	-0.65220	0.16204	0.12967	0.00000	0.01277	0.00000	0.00000	0.00000	-0.04071
1	0	0	9.15300	A	0.05898	-0.05905	0.00151	-0.00031	0.00000	-0.00086	0.00000	0.00000	0.00000	0.02724
2	0	0	1.42800	A	-0.00069	0.00530	-0.42619	-0.57010	0.00000	0.39346	0.00000	0.00000	0.00000	-4.79202
3	0	0	3.07600	A	0.00532	-0.00590	-0.18711	-0.05298	0.00000	-0.10512	0.00000	0.00000	0.00000	0.64709
2	1	0	1.15000	A	-0.00060	0.00265	0.05264	0.26196	0.00000	-0.48998	0.00000	0.00000	0.00000	-3.57204
2	1	0	2.17700	A	0.00073	-0.00035	-0.12751	0.08004	0.00000	-0.20932	0.00000	0.00000	0.00000	1.12624
2	1	0	5.15200	A	-0.00024	0.00017	0.00161	0.00655	0.00000	-0.02361	0.00000	0.00000	0.00000	-0.09360
3	2	0	1.49300	A	0.00066	0.00023	-0.04200	0.03119	0.00000	-0.05950	0.00000	0.00000	0.00000	-0.30599
8	2	0	3.50000	A	-0.00092	0.00029	0.04699	0.00109	0.00000	-0.00798	0.00000	0.00000	0.00000	-0.32590
2	1	1	1.15000	A	0.00000	0.00000	0.00000	0.00000	0.35000	0.00000	-0.42023	0.29940	-0.57576	0.00000
2	1	1	2.17700	A	0.00000	0.00000	0.00000	0.00000	0.11271	0.00000	-0.05859	0.13912	-0.03126	0.00000
2	1	1	5.15200	A	0.00000	0.00000	0.00000	0.00000	0.00979	0.00000	-0.01814	0.01226	-0.02571	0.00000
3	2	1	1.49300	A	0.00000	0.00000	0.00000	0.00000	-0.03094	0.00000	0.11791	0.03687	0.08192	0.00000
8	2	1	3.50000	A	0.00000	0.00000	0.00000	0.00000	-0.05923	0.00000	0.08521	-0.02067	-0.00837	0.00000
8	2	2	3.50000	A	0.00008	-0.00024	-0.03311	-0.09968	0.00000	0.05120	0.00000	0.00000	0.00000	0.05208
2	1	-1	1.15000	A	0.00000	0.00000	0.00000	0.00000	-0.35000	0.00000	0.42023	0.29940	-0.57576	0.00000
2	1	-1	2.17700	A	0.00000	0.00000	0.00000	0.00000	-0.11271	0.00000	0.05859	0.13912	-0.03126	0.00000
2	1	-1	5.15200	A	0.00000	0.00000	0.00000	0.00000	-0.00979	0.00000	0.01814	0.01226	-0.02571	0.00000
3	2	-1	1.49300	A	0.00000	0.00000	0.00000	0.00000	0.03094	0.00000	-0.11791	0.03687	0.08192	0.00000
8	2	-1	3.50000	A	0.00000	0.00000	0.00000	0.00000	0.05923	0.00000	-0.08521	-0.02067	-0.00837	0.00000
8	2	-2	3.50000	A	0.00008	-0.00024	-0.03311	-0.09968	0.00000	0.05120	0.00000	0.00000	0.00000	0.05208
1	0	0	5.38200	B	0.65211	0.65225	0.16204	-0.12967	0.00000	0.01278	0.00000	0.00000	0.00000	0.04072
1	0	0	9.15300	B	0.05898	0.05905	0.00151	0.00031	0.00000	-0.00086	0.00000	0.00000	0.00000	-0.02725
2	0	0	1.42800	B	-0.00069	-0.00530	-0.42621	0.57010	0.00000	0.39347	0.00000	0.00000	0.00000	4.79202
3	0	0	3.07600	B	0.00532	0.00590	-0.18711	0.05298	0.00000	-0.10512	0.00000	0.00000	0.00000	-0.64707
2	1	0	1.15000	B	-0.00060	-0.00265	0.05263	-0.26196	0.00000	-0.48998	0.00000	0.00000	0.00000	3.57201
2	1	0	2.17700	B	0.00073	0.00035	-0.12751	-0.08004	0.00000	-0.20932	0.00000	0.00000	0.00000	-1.12621
2	1	0	5.15200	B	-0.00024	-0.00017	0.00161	-0.00655	0.00000	-0.02361	0.00000	0.00000	0.00000	0.09359
3	2	0	1.49300	B	0.00066	-0.00023	-0.04200	-0.03119	0.00000	-0.05950	0.00000	0.00000	0.00000	0.30603
8	2	0	3.50000	B	-0.00092	-0.00029	0.04698	-0.00108	0.00000	-0.00798	0.00000	0.00000	0.00000	0.32582
2	1	1	1.15000	B	0.00000	0.00000	0.00000	0.00000	0.35000	0.00000	0.42023	0.29940	0.57576	0.00000
2	1	1	2.17700	B	0.00000	0.00000	0.00000	0.00000	0.11271	0.00000	0.05859	0.13912	0.03126	0.00000
2	1	1	5.15200	B	0.00000	0.00000	0.00000	0.00000	0.00979	0.00000	0.01814	0.01226	0.02571	0.00000
3	2	1	1.49300	B	0.00000	0.00000	0.00000	0.00000	-0.03094	0.00000	-0.11792	0.03687	-0.08192	0.00000
8	2	1	3.50000	B	0.00000	0.00000	0.00000	0.00000	-0.05923	0.00000	-0.08521	-0.02067	0.00837	0.00000
8	2	2	3.50000	B	0.00008	0.00024	-0.03311	0.09968	0.00000	0.05120	0.00000	0.00000	0.00000	-0.05207
2	1	-1	1.15000	B	0.00000	0.00000	0.00000	0.00000	-0.35000	0.00000	-0.42023	0.29940	0.57576	0.00000
2	1	-1	2.17700	B	0.00000	0.00000	0.00000	0.00000	-0.11271	0.00000	-0.05859	0.13912	0.03126	0.00000
2	1	-1	5.15200	B	0.00000	0.00000	0.00000	0.00000	-0.00979	0.00000	-0.01814	0.01226	0.02571	0.00000
3	2	-1	1.49300	B	0.00000	0.00000	0.00000	0.00000	0.03094	0.00000	0.11792	0.03687	-0.08192	0.00000
8	2	-1	3.50000	B	0.00000	0.00000	0.00000	0.00000	0.05923	0.00000	0.08521	-0.02067	0.00837	0.00000
8	2	-2	3.50000	B	0.00008	0.00024	-0.03311	0.09968	0.00000	0.05120	0.00000	0.00000	0.00000	-0.05207
Orbital Energies, hartrees					-11.1953	-11.1937	-1.0049	-0.7574	-0.6103	-0.5405	-0.4618	-0.3560	0.1780	0.3960

Total energy = -77.5537 hartrees.

Potential energy = -155.080 hartrees.

TABLE XXIII. TCE Wave Function for Twisted 90° Ethylene

Basis Functions			Orbital Exponent	Center	Orbital Coefficients									
n	l	m			C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)
1	0	0	5.38200	A	0.64917	-0.65517	0.16177	0.13068	0.00000	0.01393	0.00000	0.00000	0.00000	-0.04016
1	0	0	9.15300	A	0.58669	-0.59300	0.00153	-0.00020	0.00000	-0.00094	0.00000	0.00000	0.00000	0.02701
2	0	0	1.42800	A	-0.00073	0.00541	-0.42559	-0.57338	0.00000	0.39743	0.00000	0.00000	0.00000	-4.77885
3	0	0	3.07600	A	0.00542	-0.00603	-0.18799	-0.05750	0.00000	-0.10651	0.00000	0.00000	0.00000	0.64805
2	1	0	1.15000	A	-0.00069	0.00272	0.05645	0.25766	0.00000	-0.49648	0.00000	0.00000	0.00000	-3.56249
2	1	0	2.17700	A	0.00081	-0.00042	-0.13199	0.08018	0.00000	-0.20270	0.00000	0.00000	0.00000	1.11595
2	1	0	5.15200	A	-0.00015	0.00008	0.00212	0.00663	0.00000	-0.02415	0.00000	0.00000	0.00000	-0.09130
8	2	0	1.49300	A	0.00664	0.00025	-0.04390	0.03232	0.00000	-0.06379	0.00000	0.00000	0.00000	-0.29487
3	2	0	3.50000	A	-0.00095	0.00028	0.04939	-0.00011	0.00000	-0.01055	0.00000	0.00000	0.00000	-0.32865
2	1	1	1.15000	A	0.00000	0.00000	0.00000	0.00000	-0.26488	0.00000	0.41995	-0.18070	0.66809	0.00000
2	1	1	2.17700	A	0.00000	0.00000	0.00000	0.00000	-0.02945	0.00000	0.13132	-0.12878	0.02068	0.00000
2	1	1	5.15200	A	0.00000	0.00000	0.00000	0.00000	-0.01097	0.00000	0.01281	-0.00945	0.03093	0.00000
3	2	1	1.49300	A	0.00000	0.00000	0.00000	0.00000	0.07682	0.00000	-0.01423	-0.07541	-0.12105	0.00000
8	2	1	3.50000	A	0.00000	0.00000	0.00000	0.00000	0.06191	0.00000	-0.06922	-0.01998	-0.04047	0.00000
8	2	2	3.50000	A	0.00022	-0.00008	-0.05715	-0.05576	0.00000	0.07025	0.00000	0.00000	0.00000	0.39802
2	1	-1	1.15000	A	0.00000	0.00000	0.00000	0.00000	0.43079	0.00000	-0.36131	-0.55971	0.16999	0.00000
2	1	-1	2.17700	A	0.00000	0.00000	0.00000	0.00000	0.15361	0.00000	-0.04606	-0.04886	0.10119	0.00000
2	1	-1	5.15200	A	0.00000	0.00000	0.00000	0.00000	0.01282	0.00000	-0.01275	-0.02443	0.00973	0.00000
3	2	-1	1.49300	A	0.00000	0.00000	0.00000	0.00000	-0.03016	0.00000	0.08877	0.11092	0.04161	0.00000
8	2	-1	3.50000	A	0.00000	0.00000	0.00000	0.00000	-0.06756	0.00000	0.06348	0.04473	0.02137	0.00000
8	2	-2	3.50000	A	0.00013	-0.00013	-0.05187	-0.06143	0.00000	0.08530	0.00000	0.00000	0.00000	0.03700
1	0	-2	5.38200	B	0.64915	0.64925	0.16177	-0.13068	0.00000	0.01394	0.00000	0.00000	0.00000	0.04017
1	0	0	9.15300	B	0.58672	0.58676	0.00153	0.00000	0.00000	-0.00094	0.00000	0.00000	0.00000	-0.02701
2	0	0	1.42800	B	-0.00078	-0.00540	-0.42562	0.57338	0.00000	0.39742	0.00000	0.00000	0.00000	4.77885
3	0	0	3.07600	B	0.00547	0.00598	-0.18798	0.05749	0.00000	-0.10651	0.00000	0.00000	0.00000	-0.64805
2	1	0	1.15000	B	-0.00072	-0.00272	0.05644	-0.25767	0.00000	-0.49647	0.00000	0.00000	0.00000	3.56247
2	1	0	2.17700	B	0.00082	0.00041	-0.13199	-0.08019	0.00000	-0.20270	0.00000	0.00000	0.00000	-1.11594
2	1	0	5.15200	B	-0.00015	-0.00008	0.00211	-0.00663	0.00000	-0.02415	0.00000	0.00000	0.00000	0.09130
3	2	0	1.49300	B	0.00664	-0.00028	-0.04390	-0.03232	0.00000	-0.06379	0.00000	0.00000	0.00000	0.29487
8	2	0	3.50000	B	-0.00095	-0.00027	0.04939	0.00011	0.00000	-0.01054	0.00000	0.00000	0.00000	0.32865
2	1	1	1.15000	B	0.00000	0.00000	0.00000	0.00000	0.26487	0.00000	0.41993	-0.18070	-0.66809	0.00000
2	1	1	2.17700	B	0.00000	0.00000	0.00000	0.00000	0.02946	0.00000	0.13131	-0.12878	-0.02068	0.00000
2	1	1	5.15200	B	0.00000	0.00000	0.00000	0.00000	0.01097	0.00000	0.01281	-0.00945	-0.03093	0.00000
3	2	1	1.49300	B	0.00000	0.00000	0.00000	0.00000	-0.07682	0.00000	-0.01422	-0.07541	0.12105	0.00000
8	2	1	3.50000	B	0.00000	0.00000	0.00000	0.00000	-0.06192	0.00000	-0.06921	-0.01997	0.04047	0.00000
8	2	2	3.50000	B	-0.00022	-0.00007	0.05715	-0.05576	0.00000	-0.07024	0.00000	0.00000	0.00000	0.39801
2	1	-1	1.15000	B	0.00000	0.00000	0.00000	0.00000	0.43043	0.00000	0.36627	0.55971	0.16999	0.00000
2	1	-1	2.17700	B	0.00000	0.00000	0.00000	0.00000	0.15362	0.00000	0.04604	0.04886	0.10119	0.00000
2	1	-1	5.15200	B	0.00000	0.00000	0.00000	0.00000	0.01283	0.00000	0.01275	0.02443	0.00973	0.00000
3	2	-1	1.49300	B	0.00000	0.00000	0.00000	0.00000	-0.03017	0.00000	-0.08877	-0.11093	0.04162	0.00000
8	2	-1	3.50000	B	0.00000	0.00000	0.00000	0.00000	-0.06756	0.00000	-0.06347	-0.04472	0.02136	0.00000
8	2	-2	3.50000	B	-0.00013	-0.00013	0.05187	-0.06143	0.00000	-0.08530	0.00000	0.00000	0.00000	0.03700
Orbital Energies, hartrees					-11.1006	-11.1891	-1.0065	-0.7464	-0.5675	-0.5457	-0.5385	-0.2381	0.0805	0.3970

Total energy = -77.3900 hartrees.

Potential energy = -155.078 hartrees.

TABLE XXIV. Computed Molecular Properties^a for Planar and Twisted 90° Ethylene

Property	Planar Configuration	Twisted 90° Configuration	Experimental Result	Property	Planar Configuration	Twisted 90° Configuration	Experimental Result
Total energy	-77.5537	-77.3900	-	Z_a^2	72.3470	72.5104	-
Virial theorem	-2.00035	-1.99617	-	X^2	32.2978	32.0392	-
Identity	15.9998	15.9941	-	η	3.89420×10^{-5}	-5.20892×10^{-3}	-
$\text{Sin}^2(\alpha/r_a)$	11.1417	11.1544	-	Ionization potential ^b	0.3560	0.2381	0.3852 ^c
$\text{Cos}^2(\alpha/r_a)$	7.55424	7.55612	-	$\text{Sin}^2(\alpha/r_b)$	-	11.1522	-
$3Z^2 - r_a^2$	112.396	112.982	-	$\text{Cos}^2(\alpha/r_b)$	-	7.55618	-
r_a	18.6960	18.7105	-	$3Z^2 - r_b^2$	-	113.135	-
Z	4.71442×10^{-5}	-1.49954×10^{-2}	-	$1-r_b$	-	18.7084	-
ξ	27.9170	27.8951	-	r_b^2	-	104.626	-
r_a^2	104.645	104.550	-	Z_b^2	-	72.5869	-

^aValues in atomic units.^bComputed using Koopmans' approximation.^cFor the planar configuration.⁷¹

TABLE XXV. Calculated Energies for Planar and Twisted 90° Ethylene

Expectation Value, hartrees				Expectation Value, hartrees			
Planar Configuration		Twisted 90° Configuration		Planar Configuration		Twisted 90° Configuration	
Total energy	-77.5537	-77.3900		V_{vdw}	-23.6544	-23.5788	
T^a	77.5263	77.6879		V_{ee}	58.6966	58.7120	
V_i	-155.080	-155.078		V_{nn}	33.3824	33.3670	
V_{ne}	-247.159	-247.157		V_{IT}	-2.00035	-1.99616	

^aThe symbols used in this table are defined on p. 10.

D. Results for Planar Configuration

To determine the error in the two-center expansion results, the Hartree-Fock energy had to be estimated. Using the results obtained for carbon molecule, acetylene, and planar ethylene by Whitten et al.,⁶⁰ we made the following estimate:

$$\begin{aligned} E_{\text{error in } C_2} &= E_{\text{HF}}^{73} - E_{\text{Whitten}} \\ &= -75.4062 - (-75.35) \\ &= -0.0562 \text{ hartree;} \end{aligned} \tag{5.4}$$

$$\begin{aligned} E_{\text{error in } C_2H_2} &= E_{\text{HF}} - E_{\text{Whitten}} \\ &= -76.8540 - (-76.7916) \\ &= -0.0624 \text{ hartree.} \end{aligned} \tag{5.5}$$

If the error in the carbon-carbon skeleton is assumed constant between carbon molecule and acetylene, the error per hydrogen may be defined as

$$\begin{aligned} E_{\text{error/hydrogen}} &= \frac{E_{\text{error } C_2H_2} - E_{\text{error } C_2}}{2} \\ &= \frac{-0.0624 - (-0.0562)}{2} \\ &= -0.0062/2 = -0.0031 \text{ hartree.} \end{aligned} \tag{5.6}$$

The Hartree-Fock energy for ethylene is then

$$\begin{aligned} E_{\text{HF } C_2H_4} &= E_{\text{Whitten}} + E_{\text{error } C_2} \\ &\quad + 4 E_{\text{error/hydrogen}} \\ &= -78.001 + (-0.0562) + 4(-0.0031) \\ &= -78.07 \text{ hartrees.} \end{aligned} \tag{5.7}$$

This is approximately 0.15 hartree higher than Hollister and Sinanoglu's⁷² estimate of -78.2242 hartrees for the Hartree-Fock value. However, Hollister and Sinanoglu's estimate for acetylene was -76.96, or approximately 0.10 hartree too low; therefore, this estimate for ethylene is quite reasonable.

The error in the TCE calculation is then

$$\begin{aligned}
 E_{\text{error}} &= E_{\text{HF}} - E_{\text{TCE}} \\
 &= -78.07 - (-77.55) \\
 &= -0.52 \text{ hartree.}
 \end{aligned} \tag{5.8}$$

The error per proton is

$$\begin{aligned}
 E_{\text{error/proton}} &= \frac{E_{\text{error}}}{4} = -0.52/4 \\
 &= -0.13 \text{ hartree,}
 \end{aligned} \tag{5.9}$$

which is approximately twice as large as the error obtained in the TCE calculation for acetylene. If the basis set were fully optimized, the upper limit to the calculation would be

$$\begin{aligned}
 E_{\text{TCE limit}} &\approx E_{\text{HF}} - E_{\text{error carbon-carbon}} - 4 E_{\text{error/proton}} \\
 &\approx -78.07 - (-0.053) - 4(-0.077/2) \\
 &\approx -77.86 \text{ hartrees.}
 \end{aligned} \tag{5.10}$$

Table XX indicates that these results only equal the minimal basis STO results. Hence, performance versus economics precluded any optimization of the basis set. It was felt, however, that the wave function obtained had all the essential characteristics of an optimized set.

The results presented in Table XX indicate that the TCE result has the highest total energy reported. It is approximately 0.3 hartree higher than the minimal STO calculations. The results for the ionization potential[‡] compare favorably with the other calculated values. Most of the calculated values are within 10% of the experimental value.

Table XXI indicates that the orbital energies agree reasonably well with the other reported calculations. The $1a_g$, $1a_u$, and $1b_{2u}$ orbital energies agree quite well but, as expected, the bonding orbitals do not agree as well.

All the orbital energies follow the same trend as that displayed in the TCE acetylene calculations. They are all higher than the correct values.^{‡‡}

[‡] Computed using Koopmans' approximation.

^{‡‡} Because the Hartree-Fock values do not exist, the best published results of Whitten are assumed correct for comparative purposes.

The charge-density contours presented in Appendix F indicate that considerable distortion has been built into the wave function. When the total densities of carbon molecule and acetylene are compared with ethylene, it is apparent that the charge distribution has gone from nearly circular contours (carbon) and ellipsoidal contours (C_2H_2) to elliptical contours that are also distorted in the x direction. The overall appearance is roughly a dog-bone shape. Examination of the a -type orbitals indicate that they also demonstrate this type of distortion. The $2a_g$ orbital appears to have the exact shape of the total density and is undoubtedly the main contributor to the overall shape. The inner b -type orbitals are slightly distorted in the direction of the protons.

The remaining b -type orbitals is the $1b_{2u}$ orbital. This is the classical π electron orbital in ethylene. Its appearance is exactly as it has been depicted in organic textbooks, namely two "sausage"-shaped clouds above and below the plane containing the carbon atoms. There is a well-defined σ - π separation on the order of 2.3 eV. This separation is about 30% smaller, however, than that reported by other calculations.

E. Results for Twisted 90° Configuration

Little data have been published on the twisted form of ethylene. The basic reason is that in this configuration the singlet state is not a pure state, because the e -type orbitals become degenerate, thereby giving rise to the two singlet states 1A and 1B . Thus, a single determinant wave function is not satisfactory. What has been reported by Kaldor and Shavitt⁶⁷ and is being reported here is a mixture of the two states. The wave function presented in Table XXII indicates that the restriction of a single determinant wave function does not allow the inner e orbitals to become degenerate. Because of this restriction, the twisting potential cannot be accurately determined without doing a double-configuration calculation.

The energy difference between the two configurations for the TCE calculation is 0.16 hartree, which compares favorably with the 0.20 hartree that Kaldor and Shavitt obtained. Kaldor and Shavitt also did a two-term configuration-interaction calculation and obtained a value of 0.13 hartree for the energy difference. The ionization potential, however, compares quite favorably with Kaldor and Shavitt's results.

Examination of the energy quantities presented in Table XXIV gives a qualitative understanding of what happened as the system was twisted. There was a decrease in the nuclear-nuclear repulsion, accompanied by a large increase in the kinetic energy, while the electronic part of the potential energy remained constant. The overall effect was therefore a net raising of the total energy. The electronic potential energy remained constant because the decrease in the nuclear-electronic contribution was compensated for by an increase in the electronic-electronic repulsion.

The charge-density contours presented in Appendix F show the removal of the hydrogen atoms from the plane of the molecule. Comparing these plots with the plots of the planar configuration, we see that the left-hand sides of the total and a-type orbitals are equivalent. The right-hand side clearly reflects the removal of the protons. This side of the plot is analogous to what would be observed if a plot was made of the plane containing the two carbon atoms and perpendicular to the plane containing the hydrogens in the planar configuration. The b symmetry orbitals are quite distorted, and only the $1b_{3u}$ orbital resembles the planar orbital on the left-hand side. In the plots for both configurations, there are no contours surrounding the hydrogen atoms.

VI. CONCLUSIONS

A. Review of the Results

The TCE method using Slater-type orbitals was characterized and documented.

TCE calculations on the hydrogen molecule from off-center positions determined the error inherent in the method, and within the constraints of the allowed basis functions ($l \leq 3$), to be 0.035 hartree per proton.

TCE-SCF wave functions for the acetylene and ethylene molecules were obtained. These molecules provided an ideal series for characterizing the method on large systems since they have a constant heavy atom skeleton with an increasing number of off-center protons.

To make this characterization for large systems, an exhaustive search for the best basis set was performed. It was apparent during this search for acetylene that economic considerations would not permit the same procedure to be used for ethylene. The wave functions obtained are therefore not strictly comparable. The major differences between the final results presented for the two systems are:

1. The acetylene wave function was constructed from a symmetry-adapted basis set,³⁰ while the ethylene wave function was constructed from a symmetryless basis set. The use of symmetry functions permitted a greater number of expansion functions to be included in the basis set for acetylene.
2. Extensive exploration and single optimization of all the orbital exponents in the acetylene basis set were performed, but no exploration or optimization of the basis set was done for ethylene.
3. Because of the more acidic nature of the protons in acetylene than in ethylene, the charge density is less in the vicinity of the protons in acetylene and therefore easier to represent.

The results obtained for these systems were -76.7240 and -77.5537 hartrees for the total energies of acetylene and planar ethylene, respectively. For these two systems, the error per proton, defined as the deviation from the Hartree-Fock value divided by the number of protons, was 0.07 and 0.13 hartree, respectively.

The orbital energies obtained for both acetylene and ethylene orbitals not involving the carbon-hydrogen bond compared favorably with other

reported calculations. The ionization potentials obtained using Koopmans' approximation were 0.3993 and 0.3560 hartree for acetylene and planar ethylene, respectively.

B. Practicality of the Method

Although the TCE results obtained for acetylene were better than the minimal-basis STO multicenter treatments, the TCE method is not proposed as a practical intermediate to full multicenter STO treatments as the OCE method has been. The primary reason is that the ratio of wave-function quality to machine time involved is quite disadvantageous for the TCE method. The reason for this is that the OCE method requires evaluation of only atomic-type (one-center) two-electron integrals, which may be evaluated very rapidly. In the TCE method, however, there are many two-center, two-electron integrals that take $\sim 10^3$ times as long to evaluate as the atomic type. The multicenter two-electron integral may take only ten times as long to evaluate as the two-center type.^{8,9} The number of two-electron integrals goes up roughly as the number of basis functions to the fourth power. For a TCE calculation, a feasible basis set, based on equal integral computation time, could therefore only be about one and one-half times as large as a full multicenter set. On the other hand, the basis set in an OCE treatment could be nearly ten times as large as the multicenter set. If a basis set of that size could be handled, the OCE results obtained would be quite good, whereas the set used for a TCE treatment would not be adequate.

C. Future Applicability

Although the method is not proposed as a practical intermediate step for the general class of molecules $H_n-A-B-H_m$, the rather good results obtained for acetylene indicate that the method could be usefully applied to ideal members of this class, namely those with only one and two protons. Furthermore, the method could be quite useful for those excited states where the charge density at the proton would be less than in the ground state. Since there is an apparent constant framework error in different geometric configurations, term energies for transitions from orbitals not involving a carbon-hydrogen bond could be quite satisfactory.

Although the TCE total energies are in general quite poor, the total charge density is apparently adequate for structure determination. The investigation of geometrical changes involving the off-center protons requires recomputation of only a few integrals, and the error subject to these changes is constant. Therefore the method is considered practical for the investigation of geometrical energy surfaces related to the movement of the protons.

Some useful and interesting future problems using the TCE technique would be:

1. The investigation of the excited states of acetylene, ethylene, and ethane. These results would provide useful information about the approximations and parameters used in semiempirical treatments of hydrocarbons.

2. The calculation of the barrier to rotation in hydrogen peroxide. This barrier height has not been completely characterized as yet, and the TCE results should be quite good because of the polarity of the bond, the need to represent only two protons, and the cancellation of error for different proton configurations.

3. The calculation of TCE wave functions for a group of hydroxides (i.e., LiOH, NaOH, KOH, ...). The trends and properties occurring while proceeding through this alkali series would probably be properly reflected.

APPENDIX A

Molecular Integrals1. Basis Functions

The basis functions χ are the complex STO's defined in Eq. 3.2. A χ is completely described by specifying the quantum numbers n , ℓ , and m and the orbital exponent ζ .

2. Coordinate System

The coordinate system used depended upon the integral being computed and was either rectangular, spherical polar, or ellipsoidal. The basis system is a right-handed rectangular system on one center and a left-handed system on the other center, as shown in Fig. A.1. The relationships between the various coordinate systems are

$$\xi = \frac{r_a + r_b}{R};$$

$$\eta = \frac{r_a - r_b}{R};$$

$$\phi = \phi_a = \phi_b;$$

$$\cos \theta_a = \frac{1 + \xi \eta}{\xi + \eta};$$

$$\cos \theta_b = \frac{1 - \xi \eta}{\xi - \eta};$$

$$\sin \theta_a = \frac{[(\xi^2 - 1)(1 - \eta^2)]^{1/2}}{\xi + \eta};$$

$$\sin \theta_b = \frac{[(\xi^2 - 1)(1 - \eta^2)]^{1/2}}{\xi - \eta}.$$

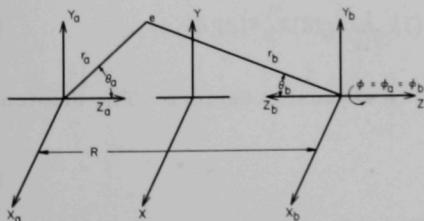


Fig. A.1

Coordinate System Used in Computing
Molecular Integrals

3. One-electron Integrals

The one-electron integrals are defined as

$$\langle \chi_p | m | \chi_q \rangle = \int \chi_p^*(1) \underline{M} \chi_q(1) dv, \quad (\text{A.1})$$

where \underline{M} may be one of the following operators: overlap (1), nuclear attraction (Z/r_i), and kinetic energy ($-\frac{1}{2}\nabla^2$); and p and q are index labels of the basis functions, which may be on either of the expansion centers. The condition for an integral to exist is that

$$mp = mq, \quad (A.2)$$

except for the nuclear attraction integrals involving the off-centers. For these integrals there are no existence tests.

4. Two-electron Integrals

There are four types of two-electron integrals.

a. One-center Type

$$\langle \chi_a \chi'_a | \chi''_a \chi'''_a \rangle = \iint \chi_a^*(1) \chi'_a(1) \frac{1}{r_{12}} \chi''_a(2) \chi'''_a(2) dv_1 dv_2, \quad (A.3)$$

where a represents one of the expansion centers, and the primes imply that the functions may be different. The condition for an integral to exist is that

$$m_a - m'_a = m''_a - m'''_a \quad (A.4)$$

and $|\ell_a - \ell'_a| - |\ell''_a - \ell'''_a|$ be even and satisfy the triangle rule.⁷⁴

b. Two-center Coulomb Type

$$\langle \chi_a \chi'_a | \chi_b \chi'_b \rangle = \iint \chi_a^*(1) \chi'_a(1) \frac{1}{r_{12}} \chi_b(2) \chi'_b(2) dv_1 dv_2, \quad (A.5)$$

where a and b are labels for the two expansion centers. The existence condition for this integral is that

$$m_a - m'_a = m_b - m'_b. \quad (A.6)$$

c. Two-center Hybrid Type

$$\langle \chi_a \chi'_a | \chi''_a \chi_b \rangle = \iint \chi_a^*(1) \chi'_a(1) \frac{1}{r_{12}} \chi''_a(2) \chi_b(2) dv_1 dv_2$$

The existence condition for this integral is that

$$m_a - m'_a = m''_a - m'_b. \quad (A.7)$$

d. Two-center Exchange Type

$$\langle \chi_a \chi_b | \chi'_a \chi'_b \rangle = \iint \chi_a^*(1) \chi_b(1) \frac{1}{r_{12}} \chi'_a(2) \chi'^*_b(2) dv_1 dv_2$$

The existence condition for this integral is that

$$m_a - m_b = m'_a - m'_b. \quad (\text{A.8})$$

Reference 28 contains a complete description of the analysis for all the diatomic integrals, and Ref. 7 describes the three-center nuclear-attraction integrals. References 29, 30, 75, and 76 describe the operating specifications for the computer programs used to calculate these integrals.

APPENDIX B

IBM-7040 Program Specifications

This program is a modified version of the IBM-7090 Homonuclear Diatomic SCF Program written by Wahl.³⁰ The major changes incorporated were:

1. The conversion of the assembly language code from FAP to MAP.
2. A new SCF routine coded in FORTRAN IV.
3. All input and output coded in FORTRAN IV.
4. Inclusion of the nuclear-attraction integrals needed for the expansion method.

The restrictions on the basis set were:

1. The quantum numbers were restricted to $n \leq 6$, and $\ell \leq 3$.
2. The total number of basis functions allowed was limited by the relationship

$$\sum_{\lambda} N_{\lambda}(N_{\lambda}+1) \leq 144,$$

where λ runs over the number of symmetries, and N_{λ} is the number of basis functions in symmetry λ .

Reference 90 contains a detailed description of the operating specifications. The program will be soon available from the Quantum Chemistry Program Exchange.

APPENDIX C

CDC-3600 Program Specifications

This program is a modified version of the CDC-3600 Heteronuclear Diatomic Program written by Wahl and Bertocini.²⁹ The input conventions and program limitations are the same for both programs and will not be repeated here.

There are three major differences between the two programs. The first difference is that the current program has been converted from a diatomic to a TCE program by the inclusion of the new nuclear attraction integrals. The second difference is that the diatomic symmetry constraints have been removed and a symmetryless program was constructed instead. A symmetryless program was chosen because all the molecules of interest could be handled without having to modify the program. Because the program is symmetryless, the maximum basis-set size permitted was 44 functions. The third and most significant difference resulted in a considerable savings of machine time per calculation. Because all basis functions were in a single symmetry (a null symmetry), the looping over them in producing the \mathcal{V} supermatrix element also produced all the necessary \mathcal{K} supermatrix elements. The latter elements, however, were not in the correct \mathcal{K} supermatrix address (namely, they were in the \mathcal{V} address), so that an algorithm had to be designed to construct a proper \mathcal{K} supermatrix from the \mathcal{V} supermatrix. Doing this, however, eliminated the need to independently compute the \mathcal{K} supermatrix, thereby cutting the integral computation time nearly in half.

The major disadvantage to this type of program occurs in the SCF procedure. Because the basis set is quite large, the time per SCF iteration increases substantially, and because it is symmetryless, no account is made for degenerate orbitals. A new convergence scheme had to be adopted for these orbitals. For very large calculations, on the order of the size of the ethylene basis set, the rate of convergence becomes very slow and the rate-determining step in the calculation becomes the SCF procedure.

APPENDIX D

TCE Wave Functions for Acetylene

TABLE D.1. TCE Wave Functions for Acetylene as a Function of the Carbon-Carbon Internuclear Separation

R C-C, bohrs	2.100	2.200	2.2267	2.281	2.400	6.000
R C-H, bohrs	2.002	2.002	2.002	2.002	2.002	2.002
Total energy, hartrees	-76.7142	-76.7256	-76.7267	-76.7240	-76.7084	-75.8109
Symmetry Basis Functions	\log Orbital Coefficients					
1S	5.32646	0.89701	0.89724	0.89728	0.89733	0.89743
1S	8.65300	0.10908	0.10922	0.10926	0.10932	0.10946
2S	1.57656	-0.00137	-0.00111	-0.00104	-0.00088	-0.00053
3S	3.87600	0.00684	0.00619	0.00601	0.00563	0.00484
2P	1.13634	0.0075	0.0071	0.0071	0.0075	0.0073
2P	2.07700	0.00198	0.00169	0.00160	0.00140	0.00100
2P	3.55200	-0.00127	-0.00129	-0.00122	-0.00103	0.00215
6P	2.75540	-0.00168	-0.00147	-0.00141	-0.00129	-0.00100
3d	1.49307	0.00443	0.00363	-0.00346	0.00316	0.00265
6d	2.43374	-0.00424	-0.00346	-0.00328	-0.00295	-0.00252
4f	1.70754	0.00004	-0.00005	-0.00005	-0.00001	0.00001
6f	2.80000	0.00000	0.00000	0.00000	-0.00013	-0.00006
Orbital energy, hartrees	-11.1952	-11.2117	-11.2162	-11.2249	-11.2438	-11.3997
$2\sigma_g$ Orbital Coefficients						
1S	5.32646	0.23519	0.22867	0.22756	0.22595	0.22475
1S	8.65300	0.01511	0.01507	0.01473	0.01386	0.01141
2S	1.57656	-0.39940	-0.42950	-0.43874	-0.43970	-0.43737
3S	2.87600	-0.42832	-0.41348	-0.40747	-0.39302	-0.35391
2P	1.13634	-0.05079	-0.06043	-0.06413	-0.07272	-0.09569
2P	2.07700	-0.020802	-0.19622	-0.19178	-0.18097	-0.14981
2P	3.55200	-0.03073	-0.02238	-0.02048	-0.01706	-0.01180
6P	2.75540	0.15555	0.16156	0.16290	0.16552	0.17127
3d	1.49307	-0.09355	-0.10081	-0.10357	-0.10865	-0.12107
6d	2.43374	0.10073	0.10062	0.10006	0.09818	0.09078
4f	1.70754	-0.02020	-0.02369	-0.02467	-0.02663	-0.03089
6f	2.80000	0.07435	0.08228	0.08408	0.08736	0.09275
Orbital energy, hartrees	-1.04335	-1.02848	-1.02443	-1.01897	-0.99738	-0.86630
$3\sigma_g$ Orbital Coefficients						
1S	5.32646	0.09601	0.07970	0.07495	0.06525	0.04543
1S	8.65300	-0.03633	-0.02999	-0.02806	-0.02399	-0.01521
2S	1.57656	0.36569	0.36722	0.36907	0.37363	0.38257
3S	2.87600	0.34662	0.28033	0.26174	0.22042	0.12443
2P	1.13634	-0.46892	-0.41125	-0.39408	-0.35808	-0.27977
2P	2.07700	-0.27878	-0.27907	-0.28222	-0.29219	-0.32643
2P	3.55200	-0.08591	-0.08870	-0.08868	-0.08768	-0.08687
6P	2.75540	-0.50418	-0.49927	-0.48425	-0.47324	-0.44850
3d	1.49307	-0.05774	-0.01967	-0.00921	0.01157	0.05149
6d	2.43374	-0.07234	-0.07709	-0.07643	-0.07274	-0.06615
4f	1.70754	-0.00729	0.00961	0.01354	0.02006	0.03268
6f	2.80000	-0.23621	-0.24567	-0.24650	-0.24612	-0.23811
Orbital energy, hartrees	-0.65832	-0.65849	-0.65831	-0.65752	-0.65451	-0.40220
$1\sigma_u$ Orbital Coefficients						
1S	5.34615	0.90912	0.00137	0.90900	0.90901	0.90908
1S	8.85300	0.09840	0.90901	0.90851	0.90854	0.90859
2S	1.22800	-0.00194	0.09844	0.00099	0.00263	0.00684
3S	2.82038	0.00580	0.00027	0.00514	0.00484	0.00416
2P	1.41437	-0.00198	0.00528	0.00094	0.00073	0.00167
2P	1.96481	0.00302	0.00018	0.00080	-0.00056	-0.00454
2P	3.20090	-0.00195	-0.00164	-0.00152	-0.00125	-0.00051
3d	1.45000	0.00091	0.00105	0.00112	0.00129	0.00185
4f	1.80974	0.00002	0.00002	0.00003	0.00004	0.00013
Orbital energy, hartrees	-11.1881	-11.2067	-11.2117	-11.2211	-11.2412	-11.3996
$2\sigma_u$ Orbital Coefficients						
1S	5.34615	0.26545	0.25893	0.25675	0.25191	0.24049
1S	8.85300	-0.02917	-0.02541	-0.02429	-0.02194	-0.01671
2S	1.22800	0.72711	0.72711	0.74374	0.76658	0.77956
3S	2.82038	-0.00789	-0.07049	-0.09420	-0.12914	-0.20010
2P	1.41437	1.92622	2.06256	2.09058	2.13787	2.20449
2P	1.96481	-0.78607	-0.89732	-0.92229	-0.96752	-1.04598
2P	3.20090	0.12042	0.13740	0.14149	0.14928	0.16431
3d	1.45000	0.07349	0.08306	0.08522	0.08902	0.09554
4f	1.80974	0.21582	0.21001	0.20866	0.20615	0.20187
Orbital energy, hartrees	-0.72715	-0.73589	-0.73819	-0.74270	-0.75235	-0.84860
$1\pi_u$ Orbital Coefficients						
2P	1.17024	0.46708	0.49116	0.49733	0.50965	0.53520
2P	2.00770	0.36725	0.34984	0.34535	0.33535	0.31770
2P	4.85200	0.06316	0.06517	0.06610	0.06778	0.07028
2P	5.75000	-0.02044	-0.02209	-0.02282	-0.02379	-0.02474
3d	2.53462	0.03549	0.03258	0.03183	0.03032	0.02716
4f	2.60000	0.02029	0.01977	0.01964	0.01941	0.01896
Orbital energy, hartrees	-0.42454	-0.41074	-0.40731	-0.40043	-0.38658	-0.23950

TABLE D.II. TCE Wave Function for Acetylene as a Function of the Carbon-Hydrogen Internuclear Separation

R C-C, bohrs	2.281	2.281	2.281	2.281
R C-H, bohrs	1.800	1.900	2.100	6.000
Total energy, hartrees	-76.6943	-76.7172	-76.7177	-75.8631

Symmetry Basis Functions	$1\sigma_g$ Orbital Coefficients			
1S	5.32646	0.89739	0.89740	0.89733
1S	8.65300	0.18922	0.18927	0.18946
2S	1.57656	-0.00121	-0.00114	-0.00074
3S	2.87600	0.00635	0.00617	0.00533
2P	1.13634	0.00029	0.00041	0.00093
2P	2.07700	0.00130	0.00147	0.00143
2P	3.55200	-0.00120	-0.00123	-0.00124
6P	2.76540	-0.00106	-0.00124	-0.00136
3d	1.49307	0.00374	0.00399	0.00463
6d	2.43374	-0.00360	-0.00332	-0.00272
4f	1.70754	-0.00013	0.00004	0.00002
6f	2.80000	-0.00010	-0.00019	-0.00012
Orbital energy, hartrees	-11.2277	-11.2266	-11.2218	-10.91761

Symmetry Basis Functions	$2\sigma_g$ Orbital Coefficients			
1S	5.32646	0.22178	0.22424	0.22817
1S	8.65300	0.01649	0.01499	0.01260
2S	1.57656	-0.44234	-0.45195	-0.46651
3S	2.87600	-0.44060	-0.41331	-0.37218
2P	1.13634	-0.08769	-0.08665	-0.05987
2P	2.07700	-0.13081	-0.15428	-0.20144
2P	3.55200	-0.02211	-0.02011	-0.01513
6P	2.76540	0.19445	0.18218	0.14694
3d	1.49307	-0.12987	-0.11814	-0.10220
6d	2.43374	0.12617	0.13917	0.08872
4f	1.70754	-0.04184	-0.03923	-0.01770
6f	2.80000	0.11408	0.10118	0.07264
Orbital energy, hartrees	-1.03128	-1.02369	-1.00791	-0.70820

Symmetry Basis Functions	$3\sigma_g$ Orbital Coefficients			
1S	5.32646	0.07889	0.07135	0.05687
1S	8.65300	-0.02786	-0.02572	-0.02118
2S	1.57656	0.24736	0.31129	0.44015
3S	2.87600	0.30624	0.25967	0.16813
2P	1.13634	-0.23593	-0.27388	-0.45295
2P	2.07700	-0.41535	-0.36494	-0.22314
2P	3.55200	-0.06072	-0.07185	-0.10200
6P	2.76540	-0.49437	-0.49443	-0.43346
3d	1.49307	0.55851	0.53413	-0.00590
6d	2.43374	-0.13227	-0.09724	-0.04739
4f	1.70754	0.06262	0.04680	-0.01300
6f	2.80000	-0.28276	-0.24914	-0.21071
Orbital energy, hartrees	-0.70157	-0.67976	-0.63525	-0.13426

Symmetry Basis Functions	$1\sigma_u$ Orbital Coefficients			
1S	5.34615	0.90935	0.90931	0.90888
1S	8.65300	0.09835	0.09841	0.09861
2S	1.22800	0.00737	0.00703	0.00090
3S	2.82038	0.00515	0.00499	0.00473
2P	1.41437	0.00824	0.00761	0.00072
2P	1.96481	-0.00461	-0.00384	0.00090
2P	3.20090	-0.00070	-0.00079	-0.00148
3d	1.45000	0.00207	0.00198	0.00100
4f	1.80974	0.00012	0.00014	0.00001
Orbital energy, hartrees	-11.2239	-11.2229	-11.2181	-10.9140

Symmetry Basis Functions	$2\sigma_u$ Orbital Coefficients			
1S	5.34615	0.24659	0.25342	0.24893
1S	8.65300	-0.01862	-0.02162	-0.02160
2S	1.22800	0.65559	0.77176	0.79956
3S	2.82038	-0.16125	-0.14257	0.12069
2P	1.41437	1.84872	2.05936	2.17961
2P	1.96481	-0.67846	-0.86280	-1.04536
2P	3.20090	0.08980	0.12354	0.17062
3d	1.45000	0.07356	0.09046	0.08460
4f	1.80974	0.20539	0.20877	0.20133
Orbital energy, hartrees	-0.79163	-0.76755	-0.71914	-0.23020

Symmetry Basis Functions	$1\sigma_u$ Orbital Coefficients			
2P	1.17024	0.50350	0.50657	0.51279
2P	2.00770	0.34511	0.34073	0.33198
2P	4.85200	0.06202	0.06486	0.07062
2P	5.75000	-0.02001	-0.02186	-0.02568
3d	2.53462	0.02686	0.02872	0.03166
4f	2.60000	0.02115	0.02027	0.01864
Orbital energy, hartrees	-0.41075	-0.40587	-0.39443	-0.11015

APPENDIX E

Charge-density Plots for Acetylene

1. For Figs. E.1-E.7, the largest contour value plotted was $1.0 \text{ e}^-/\text{bohr}^3$, and the smallest contour value plotted was $1.95 \times 10^{-3} \text{ e}^-/\text{bohr}^3$.
2. For Figs. E.8-E.18, the carbon nucleus is located at 1.140 bohrs and the hydrogen nucleus at 3.142 bohrs.
3. For Figs. E.8-E.12, the symbols used were:
 - + for the McLean Hartree-Fock wave function,⁵⁶
 - for the TCE wave function.
 - for the McLean minimal basis-set wave function.⁵⁵
4. For Figs. E.13-E.16, the symbols used were:
 - + for the density difference between the TCE results and the McLean Hartree-Fock results.
 - for the density difference between the TCE results and the McLean minimal basis-set results.

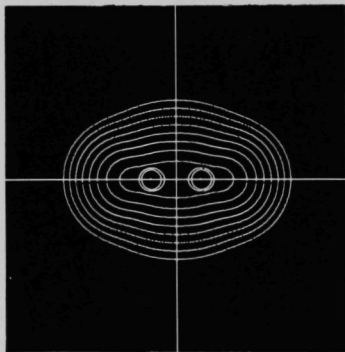


Fig. E.1. Total Charge-density
Contours for Acetylene

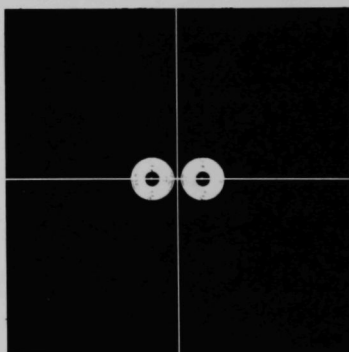


Fig. E.2. Charge-density Contours of
 $1\sigma_g$ Orbital for Acetylene

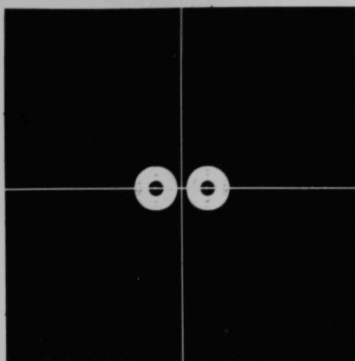


Fig. E.3. Charge-density Contours of $1\sigma_u$ Orbital for Acetylene

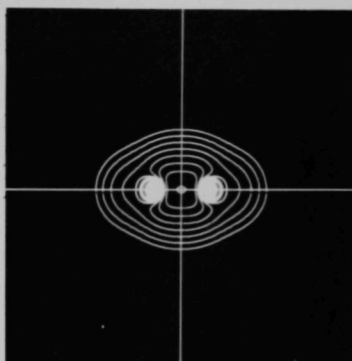


Fig. E.4. Charge-density Contours of $2\sigma_g$ Orbital for Acetylene

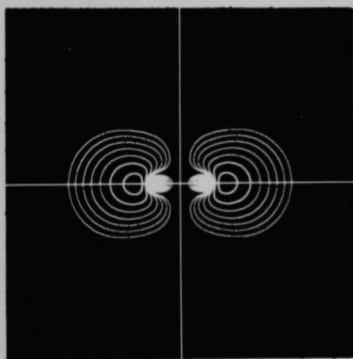


Fig. E.5. Charge-density Contours of $2\sigma_u$ Orbital for Acetylene

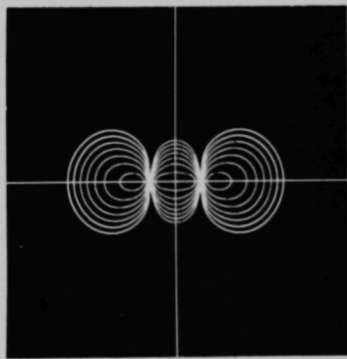


Fig. E.6. Charge-density Contours of $3\sigma_g$ Orbital for Acetylene

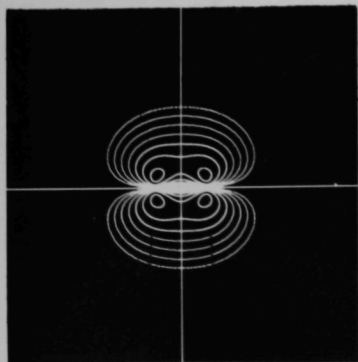


Fig. E.7
Charge-density Contours of $1\pi_u$ Orbital for Acetylene

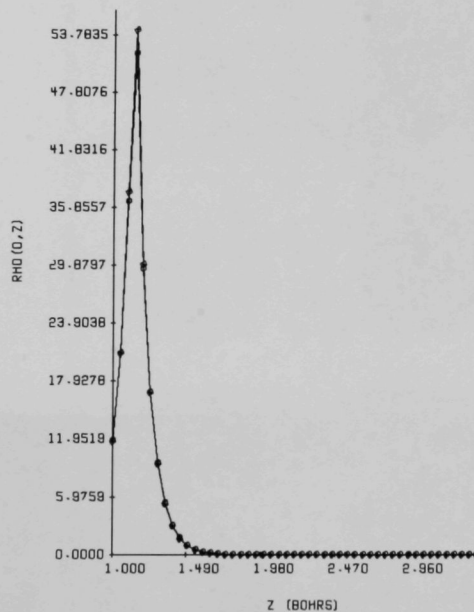


Fig. E.8. Charge-density Plots of $1\sigma_g$ Orbital for Three Acetylene Wave Functions

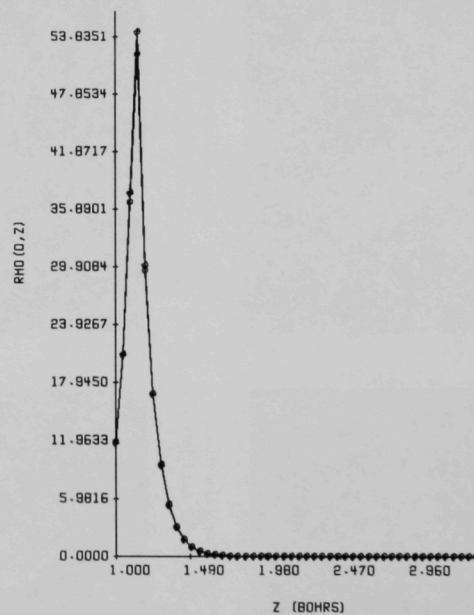


Fig. E.9. Charge-density Plots of $1\sigma_u$ Orbital for Three Acetylene Wave Functions

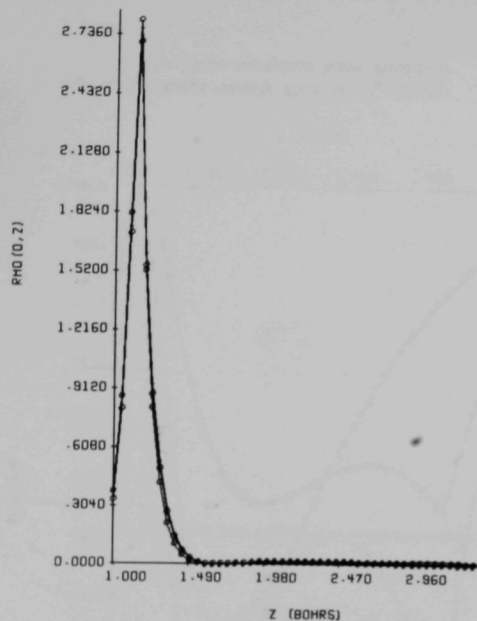


Fig. E.10. Charge-density Plots of $2\sigma_g$ Orbital for Three Acetylene Wave Functions

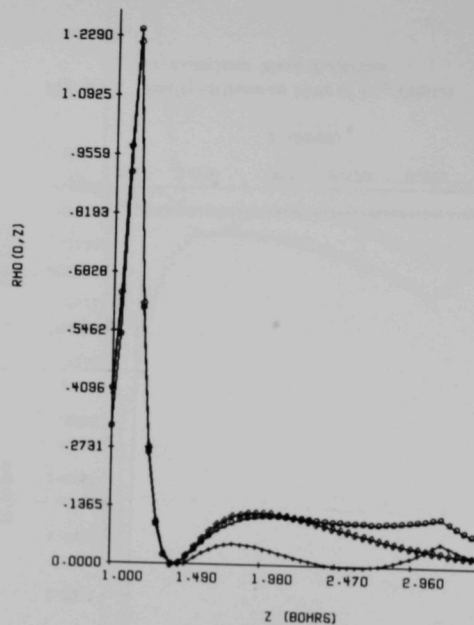


Fig. E.11. Charge-density Plots of $2\sigma_u$ Orbital for Three Acetylene Wave Functions

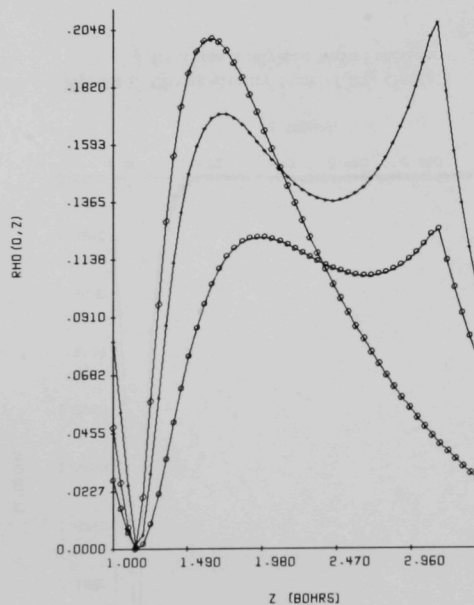


Fig. E.12. Charge-density Plots of $3\sigma_g$ Orbital for Three Acetylene Wave Functions

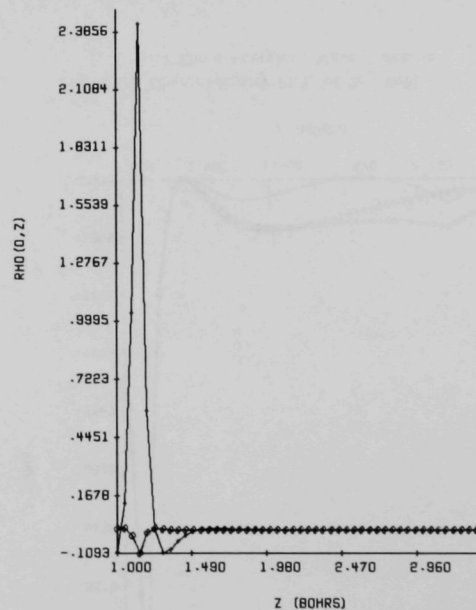


Fig. E.13. Density-difference Plots of $1\sigma_g$ Orbital for Acetylene Wave Functions

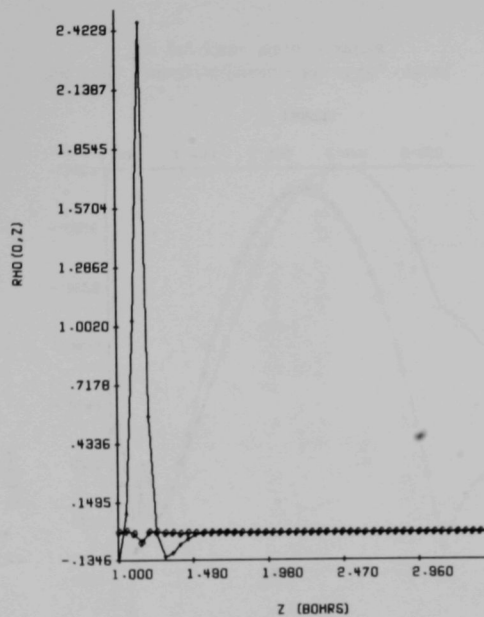


Fig. E.14. Density-difference Plots of $1\sigma_u$ Orbital for Acetylene Wave Functions

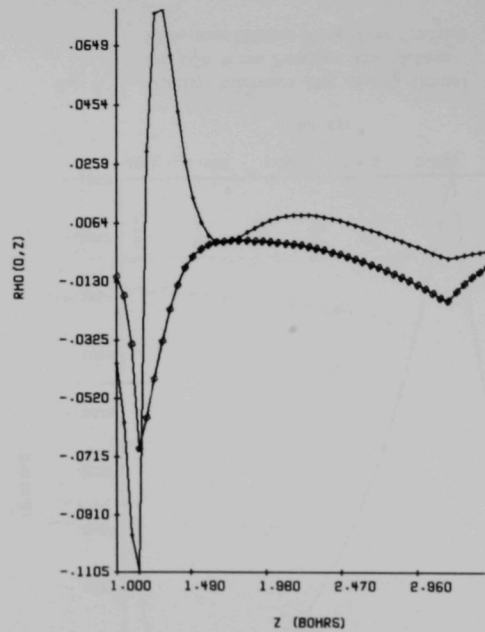


Fig. E.15. Density-difference Plots of $2\sigma_g$ Orbital for Acetylene Wave Functions

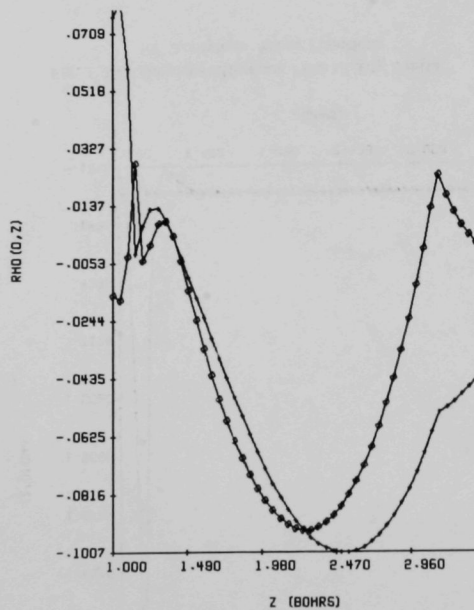


Fig. E.16. Density-difference Plots of $2\sigma_u$ Orbital for Acetylene Wave Functions

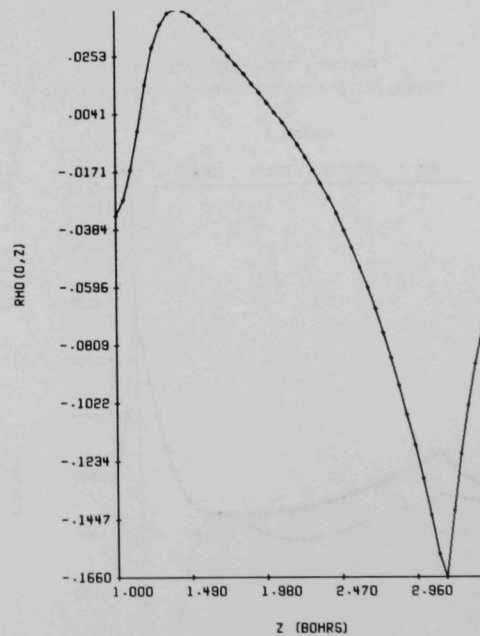


Fig. E.17. Density-difference Plot of $3\sigma_g$ Orbital for TCE Wave Function and McLean-Yoshimine Hartree-Fock Wave Function

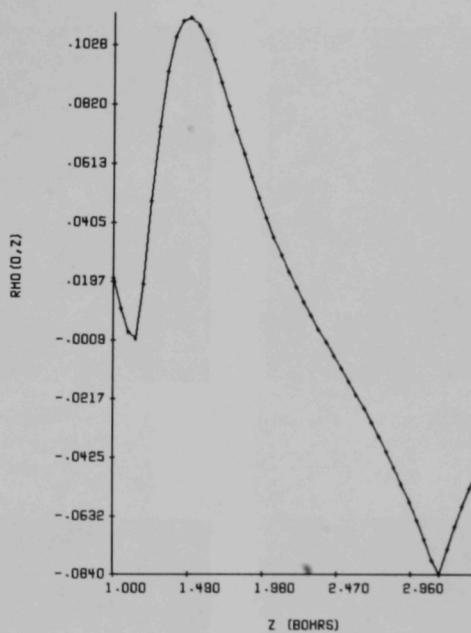


Fig. E.18. Density-difference Plot of $3\sigma_g$ Orbital
for TCE Wave Function and McLean
Minimal Basis-set Wave Function

APPENDIX F

Charge-density Contours for Ethylene

The largest contour value plotted was $1.0 \text{ e}^-/\text{bohr}^3$, and the smallest contour value plotted was $1.95 \times 10^{-3} \text{ e}^-/\text{bohr}^3$.

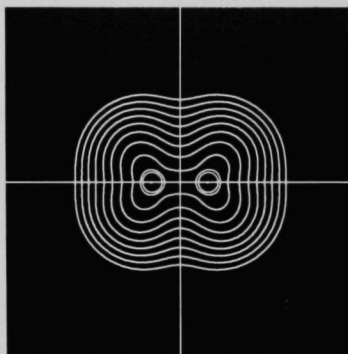


Fig. F.1. Total Charge-density Contours for Planar Ethylene

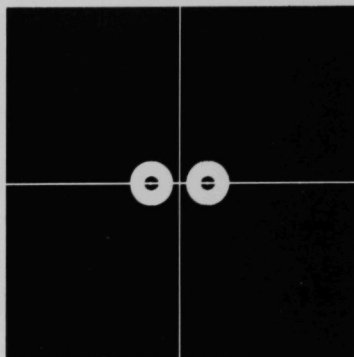


Fig. F.2. Charge-density Contours of $1a_g$ Orbital for Planar Ethylene

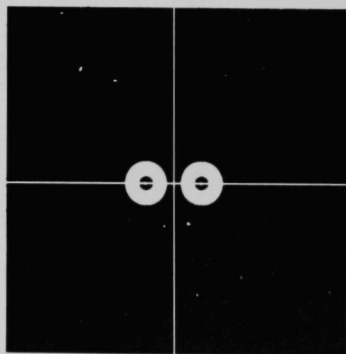


Fig. F.3. Charge-density Contours of $1a_u$ Orbital for Planar Ethylene

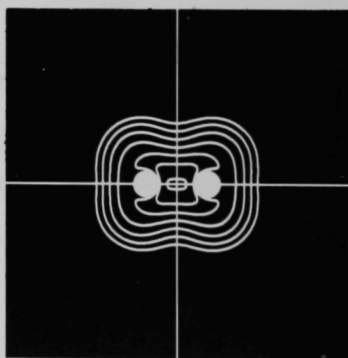


Fig. F.4. Charge-density Contours of $2a_g$ Orbital for Planar Ethylene

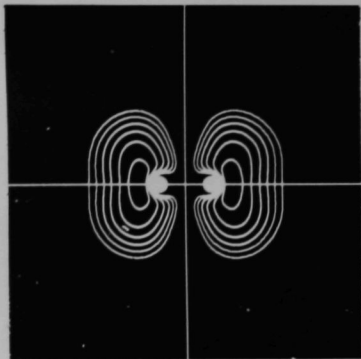


Fig. F.5. Charge-density Contours of $2a_u$ Orbital for Planar Ethylene

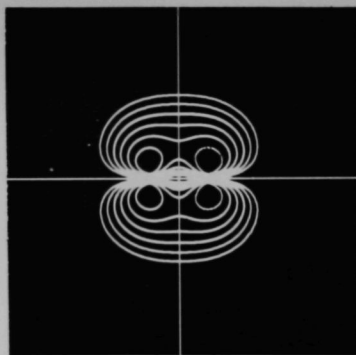


Fig. F.6. Charge-density Contours of $1b_{3u}$ Orbital for Planar Ethylene

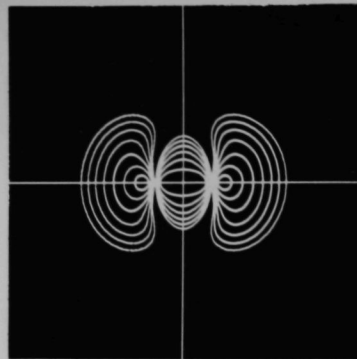


Fig. F.7. Charge-density Contours of $3a_g$ Orbital for Planar Ethylene

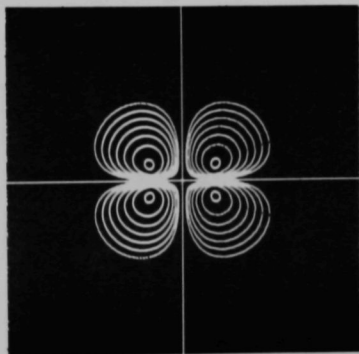


Fig. F.8. Charge-density Contours of $1b_{2g}$ Orbital for Planar Ethylene

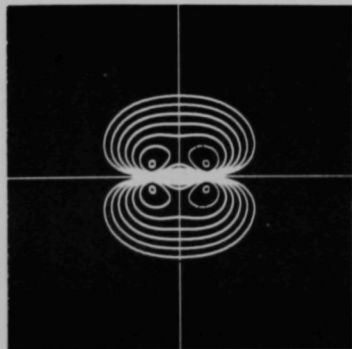


Fig. F.9. Charge-density Contours of $1b_{2u}$ Orbital for Planar Ethylene

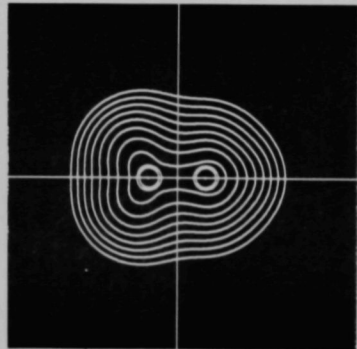


Fig. F.10. Total Charge-density Contours for Twisted 90° Ethylene

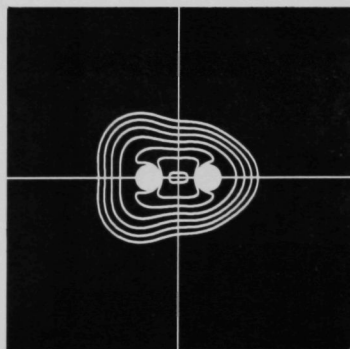


Fig. F.11. Charge-density Contours of $2a'$ Orbital for Twisted 90° Ethylene

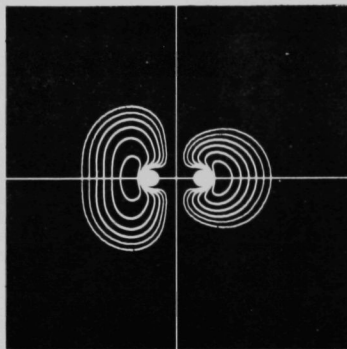


Fig. F.12. Charge-density Contours of $2a''$ Orbital for Twisted 90° Ethylene

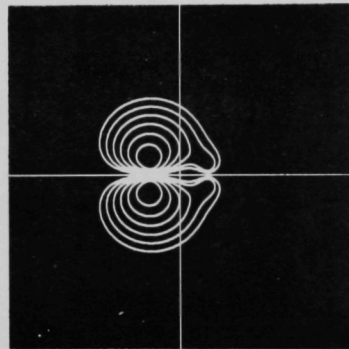


Fig. F.13. Charge-density Contours of $1e'$ Orbital for Twisted 90° Ethylene

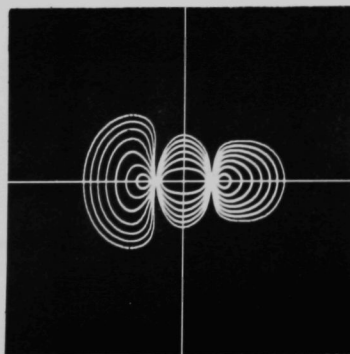


Fig. F.14. Charge-density Contours of $3a'$ Orbital for Twisted 90° Ethylene

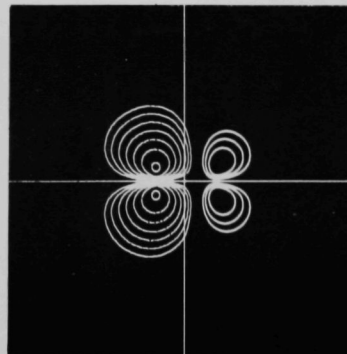


Fig. F.15. Charge-density Contours of $1e''$ Orbital for Twisted 90° Ethylene

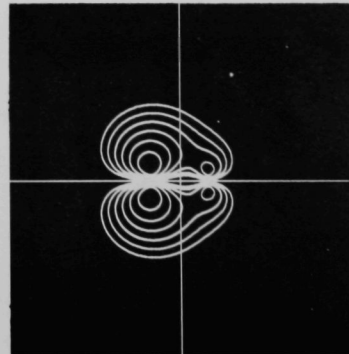


Fig. F.16. Charge-density Contours of $2e'$ Orbital for Twisted 90° Ethylene

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